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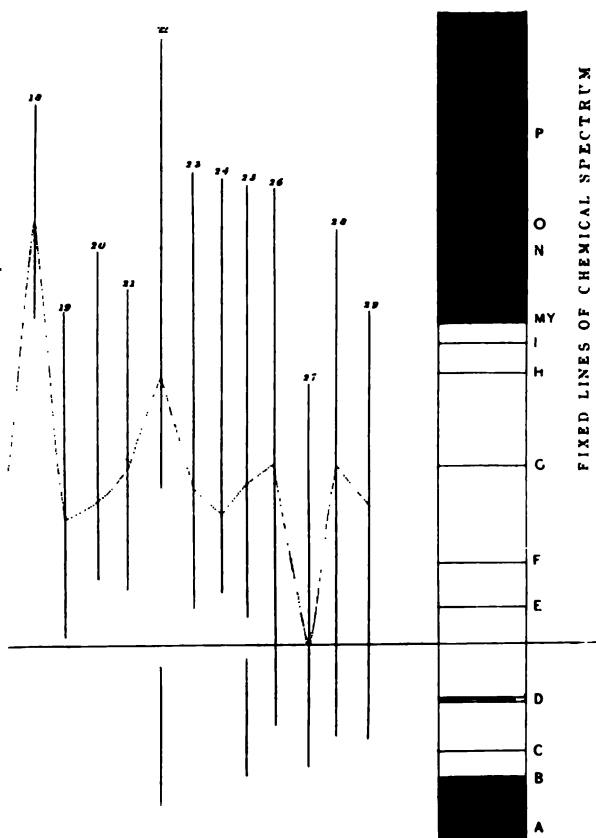




RESEARCHES  
ON  
L I G H T.







A.

ION OF ANY KIND  
NAMED

RESEARCHES  
ON  
L I G H T  
IN ITS  
CHEMICAL RELATIONS;

EMBRACING A CONSIDERATION OF ALL THE  
PHOTOGRAPHIC PROCESSES.

BY ROBERT HUNT, F.R.S.

SECOND EDITION.

LONDON:  
LONGMAN, BROWN, GREEN, AND LONGMANS.  
1854.

*143. a. 46.*



## P R E F A C E

TO

S E C O N D   E D I T I O N .

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THE constantly increasing interest in the beautiful Art of Photography, has naturally led all who practise it to desire some knowledge of the agency by which their pictorial results are produced. The chemistry of the solar radiations, or, as it has been appropriately termed, *Actino-chemistry*, is essentially a new science. The breaking up of strong chemical combinations by a power so subtile as that of the sunbeam, is amongst the most striking of the facts which claim the attention of the natural philosopher. While the physical and chemical phenomena of the solar radiations require for their investigation the aid of all the refinements of modern science.

For the purpose of placing in the hands of all who are interested in this science, a clear and satisfactory record of the progress which has been made since the publication of the First Edition of these "Researches," it has been found advisable to entirely recast the work. More than two-thirds of it has therefore been re-written, and the remaining third materially modified.

The former Edition was spoken of by some reviewers as a compilation. Since the rewards to the original investigator are but few, I feel it necessary to claim for my labours a higher position.



Before the publication of either of the Photographic processes of M. Daguerre or of Mr. Fox Talbot, while yet there were but vague rumours of the production of pictures by Solar Light, the experiments which these "Researches" record were commenced, and they have been continued almost without intermission to the present time.

Many of the Photographic processes described were the reward of my experiments. The analyses of the solar beam, determining the relation between the Light and the chemical power of the solar rays are almost entirely original. The investigations on the influence of Light on Germination and the Growth of Plants, with the practical applications which have been made of my discoveries, I can refer to with satisfaction.\* I have used the labours of other men no further than they were necessary to illustrate the subject under consideration, and each investigator will, it is hoped, find his labours recorded with careful truth.

This Edition of the Researches on Light, whatever may be its value, is the result of thousands of experiments, made at no small cost, and with a large expenditure of thought. I have aimed at the elucidation of an obscure subject; I have endeavoured to keep my mind free of all pre-conceived notions, and to read my experimental results by the illumination they afforded. It is exceedingly probable my interpretations may not be always correct, but my judgment has been founded on a most careful study of all the phenomena observed.

\* See Appendix, No. III., "On the Use of Blue Glass in accelerating Germination;" and No. IV., "On the Glass in the Palm House at the Royal Botanical Gardens at Kew."

In submitting this Volume to the public, I regret having been compelled to say thus much of myself and my labours; but the ungenerous attacks of those with whom I have ventured to differ in opinion have compelled me to the painful task.

Truth is the end we seek; and I now venture to commit these few endeavours towards its advancement to the judgment of the world, premising that this volume probably contains the record of labours, which may not be for some time renewed, my duties directing my industry into another and a sterner field of investigation.

ROBERT HUNT.

London, June 14. 1854.



## PREFACE

TO

FIRST EDITION.

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THE accumulation of facts in that department of science which immediately considers the chemical changes produced by the solar rays, has been so great, that the necessity of collecting and collating them, has been felt by all who were in the least degree interested in the progress of the inquiry. Whether I have executed this task satisfactorily or otherwise, is for the public to decide. I have endeavoured, as this is the first History of Photography which has been published, to give to every one his full share in these discoveries, which have accelerated the advancement of that art ; and although in many cases my interpretation of phenomena may differ from that given by the observers themselves ; in all, I have been most careful to adhere to their own expression of the facts.

I have, throughout the principal portion of this Work, laboured under the difficulty of being obliged to speak of photographic phenomena as resulting from the agency of LIGHT, being at the same time fully satisfied that they were to be referred to a principle which possessed none of the characters of LIGHT or HEAT, but which was intimately mixed with these elements in the solar rays. This subject is fully discussed in the third division of the Volume ; but

I refer to it now, for the purpose of explaining, that the implied contradiction is only a submission to the generally received idea, for the purpose of rendering the inquiry intelligible to every reader.

It is due from me, that I acknowledge the kind and generous assistance which, through every stage of these experimental inquiries, I have received from Sir J. F. W. Herschel. The readiness with which that philosopher has communicated his discoveries, and the free and candid manner in which he has favoured me with his views, claims this expression of my feelings, as the only way in which I can sufficiently show the value at which I estimate his liberal endeavours to assist a very humble experimentalist, in a path of inquiry in which, by his own laborious and ingenious researches, he has established his high pre-eminence. To Professor Wheatstone I am also indebted for some valuable matter connected with the early history of Photography.

ROBERT HUNT.

Falmouth, March 11. 1844.



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## INTRODUCTION.

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BACON declared, —there can be no real knowledge but that which is based on observed facts ; and the correctness of this has been admitted by all eminent thinkers since his time.

A fact new to man's knowledge—the blackening of a white salt of silver—presents itself, and naturally the discoverer seeks to find the cause to which this phenomenon is due. The salt of silver remains perfectly white so long as it is kept in darkness ; but it blackens when it is exposed to sunshine. Consequently the change of colour, which is all that was at first observed, appearing to be connected with Light, man devises an interpretation of the phenomenon—forms a hypothesis—and says, “the calx of silver separates the phlogiston from the light, and retains the superfluous phlogiston of light.” Men of science have changed their views ; but their mode of reasoning on this phenomenon is as much guided by preconceptions as was that of Scheele when he was disposed to refer the decomposition of chloride of silver to phlogiston.

Conjecture is a process common to every mind ; we all frame hypotheses as we endeavour to advance from effects to causes. The strictest inductive philosophy allows of this ; but the hypothesis must not be permitted to take the place of a theory, which is an explanation based on a large number of well-observed facts. Newton's fundamental rule was, “No more causes, nor any other causes of natural effects, ought to be admitted, but such as are both



true, and are sufficient for explaining their appearances." To account for many of the phenomena of Light, philosophers have conjectured, that the unknown *something* to which they are due has a wave motion, — that the *ether* pervading all space being set into vibration, or tremor, affects the eye with the sensation of Light. Since this hypothesis explains the largest number of luminous phenomena, it is generally received. However, it must not be forgotten, that we arrive at this hypothesis by reasoning from analogy. If we cause a stretched string to vibrate, its pulsations are communicated to the surrounding air, and the waves thus produced beat upon the auditory membrane, and produce Sound. We know the fact of the existence of the air—the fact of the vibrating cord; and if we place some peculiar arrangements of mobile bodies between the cord and the ear, we prove that the air partakes of the undulations of the string. Upon a fancied analogy, hypothesis creates the *ether*, and then sets it vibrating to produce an effect on the eye of a similar order to that which the air produces on the ear — that is, undulations in one case give rise to sound, in the other to Light. This is not the place to discuss the entire question of the undulatory hypothesis of Light; but, since attempts have been made to apply it to the phenomena exhibited in breaking up strong chemical affinities by the operation of a radiant force, it appeared necessary to place it clearly before the reader. A most eminent European thinker has written, "Notwithstanding all arbitrary suppositions, the phenomena of Light will always constitute a category *sui generis*, necessarily irreducible to any other: a light will be for ever heterogeneous to a motion or a sound."

The fact that chloride of silver darkens upon exposure to sunshine, or to daylight, is what we have to examine. We may take this simple phenomenon of change as representing all that are embraced in this Volume, the differences being only in degree. Since this white salt of silver will not darken in the absence of Light, it was reasonable that

the change should be referred to the luminous element ; hence, those pictures produced in the camera obscura by the influence of the solar rays, have been called Photographic drawings. When, however, we proceed with our examination and clearly understand all the conditions under which chloride of silver changes colour in the sunshine, we cannot fail to observe the several peculiarities following :—

1st. Those rays which give the most Light—the yellow and the orange rays—will not produce change of colour in the chloride of silver.

2nd. Those rays which have the least illuminating power—the blue and violet—produce the greatest change, and in an exceedingly short space of time.

3rd. The rays which pass through certain yellow glasses have no effect on chloride of silver.

4th. The rays which pass through very dark blue glasses rapidly change the colour.

The yellow glasses obstruct scarcely any Light ; the blue glasses may be so dark as to admit of the permeation of an exceedingly small quantity.

5th. Where there is no sensation of Light under ordinary circumstances, beyond the violet rays of the spectrum, the chemical change is speedily produced.

Reasoning upon these facts, and some others of a still more striking character, mentioned under their proper divisions, it appeared to M. Berard that “solar Light consisted of three substances” to which severally belonged “the colorific, calorific, and chemical phenomena.” This hypothesis did not however receive any support from the philosophers of his time, and the weight of several eminent names was brought in support of the opposite view. In the Historical Section I have directed attention to an experiment by the eminent Dr. Young, and I have printed in the Appendix a letter from the Rev. J. B. Reade, who strongly supports Dr. Young’s position.

An attentive consideration of Dr. Young’s experiment,

as there described, proves no more than this,—that, as in the ordinary refracted spectrum the chemical action is found at its maximum about the region of the violet rays; so in the interference spectrum, the chemical change is confined to the violet rings.

We must certainly come to the conclusion that the rays which produce the chemical changes under consideration are subject to the laws of refraction and interference like Light. But if they were Light rays, I cannot conceive why, in the yellow, and therefore most luminous rings, no chemical change occurred.

Again, M. E. Becquerel and Professor Stokes have proved that the chemically impressed spectrum—over those spaces which are more especially chemically active—exhibits inactive lines which exactly correspond with the dark lines of that same portion of the spectrum when rendered luminous. This, however, proves no more than that the cause which occasions the absorption of Light along certain lines, does, at the same time, occasion the absorption of the principle to which the chemical agency is due. This view, as will be seen in the sequel, received also the support of M. Arago, who, although most favourably predisposed to urge the theory of undulation, wherever it was possible to do so, did not fail to perceive that the phenomena of Light and chemical action were heterogeneous.

That there may exist some one all-pervading principle—an ether—which may, under different conditions of motion, give rise to effects of a dissimilar character, is a probability which is not denied; it is, however, contended that the facts observed do not support such a conjecture in connection with the chemical changes produced by the solar rays.

The undulatory theory supposes Heat—I refer entirely here to the conditions of the prismatic spectrum—to be the result of a set of vibrations of a certain length and quickness, and the ether thus vibrating is only bent, by the prism, slightly out of its path. Light is the result of

the same ether pulsating to a quicker time, consequently in shorter waves, the refraction being much greater. Chemical action is produced by a system of vibrations smaller and infinitely more rapid; while here the bending of this set of waves—the chemically active ray—is to a much greater angle than either of the others. This is the hypothesis: now take a fact. By means of two prisms, two spectra are formed, each of which produces upon chloride of silver a chemical change from the green ray to some distance beyond the visible violet. Each spectrum is now so arranged, that the inactive yellow and orange rays of one are thrown upon the most active blue and violet rays of the other. The result is, that chemical action is entirely stopped. This may be said to be due to interference; but I must confess I cannot understand upon what principle the action of rays undulating 535 millions of millions of times in a second, and producing Light, can interfere with rays vibrating 727 millions of millions of times in the same period, producing, as experiment proves, chemical change. To support the view, that Light regarded as an undulation produces chemical change, since the chemical cause must reside in—must be—the particular ray and nothing else, it is necessary to prove, that when we obliterate a coloured ray of Light, all chemical action should cease over the space which belongs to such especial ray: and also that when the luminous coloured ray is not obstructed its chemical power should still exist undiminished. Reference to the chapter devoted to the action of absorbent media will show that the blue rays, regarded as the rays to which the maximum chemical effect belongs, may be entirely obliterated without the chemical effect ceasing; and that under other conditions the blue ray may appear clear and intense in the spectrum thrown on the chloride of silver, and yet produce no chemical effect.

After many years of close experimental examination, and an equally long and careful study of the hypotheses

applied in explanation of the phenomena of Light in the first place, and subsequently to the chemical phenomena associated with Light, I cannot bring my mind to adopt the view, which refers the Photographic phenomena to the agent producing the luminous and calorific phenomena of the solar rays. As it respects Light, I am quite ready to bow to the numerous high authorities who support the undulatory hypothesis. Not so, however, with regard to the chemical radiations. Indeed, it must not be forgotten that, with the exception of Dr. Young, who reposes on a solitary experiment, and one or two men of inferior note, no one, who has examined for himself the chemical phenomena, has ever put forward the view in question.\*

Careful study of this Work will show the amount of support which the following views receive from experiment:—

Light, Heat, and chemical power come to us associated in the sunbeam.

No two of the phenomena produced by these agencies are similar.

They do not obey the same laws of refraction, although they appear to be capable of undergoing the conditions of polarisation, &c.

Material bodies act differently upon them.

A diaphanous body for Light may be perfectly opaque for the chemical power, and a medium *nearly* opaque for Light may be quite transparent to the chemical principle. Heat not being the subject under examination, does not require any particular mention; the power that we possess, however, of separating Light and Heat will be described in the Appendix. Regarding, therefore, the chemical principle as something distinct from either Light or Heat, it became necessary to establish some term by which it should be recognised.

In the first edition of these “Researches” the following

\* See Appendix, No. II.

passage occurs: it is quoted for the purpose of showing that the above views have not been hastily adopted, and to give the origin of the term ACTINISM, which has been almost universally adopted:—

“The science of Thermotics (*Whewell*), or of Thermochroology (*Melloni*), is considered of sufficient importance to have its nomenclature; and M. Melloni, in a paper published in the ‘Bibliothèque Universelle de Genève,’ October, 1841, has entered very fully into the matter. It is therefore essential to the successful prosecution of our inquiries that the third class of phenomena, which we have been particularly engaged in the consideration of, should have a term by which it might be distinguished. Sir John Herschel, in his memoir ‘On the Chemical Action of the Rays of the Solar Spectrum,’ used the epithet *Actinograph* to indicate an instrument of a very ingenious kind, devised by him for registering the different degrees of chemical power accompanying the solar Light during the day. . . . We might therefore, upon the strength of this authority, adopt the substantive *ἄκτιν* (ray), and give some compound term formed from this radical to indicate this principle accompanying the other solar rays. There is, it must be admitted, some difficulty involved in the adoption of such a term, as it will apply to any radiant power, whether Light, Heat, or Photographic energy.”—Under this impression, I proposed to adopt such a term as *ενεργημα*, ENERGEMA (energy), which was slightly modified and converted into ENERGIA, to which it was thought, if desirable, the substantive *ray*, for the purpose of expressing the agent more correctly, might be prefixed, thus making ACTINERGIA.

At the meeting of the British Association at York, the value of this term was discussed. Sir John Herschel had communicated a paper designated as “Contributions to Actino-Chemistry,” which he spoke of as “the newly-created science;” and it was thought advisable by several members of the Chemical Section to adopt the term Ac-

TINISM instead of *energia*, when desiring to speak of the chemical power of the sunbeam.

It may be necessary to remark, that the chemical powers belonging to LIGHT and HEAT are scarcely to be confounded with ACTINISM. Light does, by exciting vitality in living organisms, produce chemical decomposition; and there is reason for believing that on dead organic matter *Light* acts chemically, but never on inorganic masses. HEAT, as a radiant force, also produces changes of a peculiar kind, which will be fully described; but these are broadly distinguished from the effects produced by ACTINISM. These remarks and this explanation of my views were thought necessary, owing to the severity with which my opinions have been judged: I have only now to submit them and the following "Researches" to the judgment of the reader, premising that I am quite prepared to resign the views advocated, the moment one conclusive experiment has been arrived at in support of the view that Light is the chemical agent producing Photographic phenomena.

# RESEARCHES ON LIGHT,

&c.

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## CHAPTER I.

HISTORY OF THE PROGRESS OF THE INQUIRY UNTIL THE ANNOUNCEMENT OF THE DISCOVERY OF PHOTOGRAPHY.

(1.) INVOLVED in mystery as every thing connected with the early history of our planet is, it would be entangling the subject with abortive speculations, did I offer any on those passages of the Mosaic history which narrate the creation of Light, and of the orbs of the firmament. We there find Light the creation of the first day ; and the Sun, which we are accustomed to regard as the source of Light, or the exciting mover of the luminiferous ether, as the creation of the fourth period. Regarding this, our only record of the beginning, as the true expression of the sequence of events, it does not appear that we are required to interpret this revealed word to our finite apprehensions. The origin of things is lost in the sepulchral darkness of time, into which the eye of the most gifted cannot penetrate. The Pentateuch declares in sublime conciseness, *And God said, Let there be Light, and there was Light*, Distinguishingly marking the importance of this element in the great system of Nature. The grass, the herb yielding seed, and the fruit-tree yielding fruit, owe their growth, their glowing colours, and their beauty, to the influences of the solar beams. The moving creatures of the waters — the fowl that fly above the earth in the open firmament of heaven — the cattle and the creeping thing



are directly dependent for healthful vigour, and indeed the continuance of life, on this subtile power, which appears to have given form to the chaotic earth, as it chased the darkness from the face of the deep.

(2.) An agent influencing every form of animate and inanimate creation, would necessarily excite the attention of mankind from the earliest periods. As it is by the influence of Light operating through the wonderful mechanism of the organ of vision, that a most extensive and important class of impressions are made upon the mind of man, he has, from the infancy of his days, regarded its source with feelings of wonder; and the Sun has been the object of his untutored adoration.

(3.) The uncultivated inhabitant of the wilds of nature had his moments of contemplation; and then his thoughts, travelling in the misty labyrinth of ignorance and superstition, shadowed out a great primary cause, to which he referred all the mysteries of that mighty universe of which he found himself a proud inhabitant.

The nomadic tribes of the Caucasian valleys over which spread a luxuriant vegetation, and an excess of life, could not but observe the peculiar obedience of organised creation to the influences of the changing seasons. The pastoral state was peculiarly adapted for the cultivation of those powers of the mind which elevate the individual or the mass; and in the progress of the shepherd-kings we may trace the dawning of the reign of reason, which eventually gave to a small nation the sovereignty of the known world. Men in this condition could not long remain ignorant of the dependence of all the phenomena of vegetation upon Light. The growth of the plant, the unfolding of the leaf, the formation of the flower, of the fruit and of the seed, were soon found to be under the influence of the orb of day. In spring and summer external nature was seen to grow into strength and beauty, and through autumn and winter to decline, and indeed to die. Some connection between these phenomena and the increasing and declining powers

of the sun, at an early period became evident to man; and when the innate consciousness of a creative power was struggling, through the darkness of superstitious ignorance, he, in his simplicity, gave to that orb the attributes of a god. The earliest religions of the Oriental races all bear evidence of this; and their mythologies, rich in the poetry of Nature, place one deity at the head of their polytheistic systems—the God of Heaven and of Light. In Baal and Astarte—in Zeus and Hera—in Apollo and Athena—we see alike, impersonations of Light the eternal renovator, and of Nature flourishing and decaying beneath the alternations of its power.

(4.) In the youth of mankind all natural truths were viewed through a veil, which no one dared to draw aside, or dreamed of lifting up. A beautiful poetry overspread creation, and the spirit of life was seen and worshipped in the highest and the lowliest things.

At length a philosophic spirit grew up in the mind of man: he speculated on the mysteries by which he found himself surrounded—involved himself in the mazes of metaphysics; and all his early efforts “were like the gropings of the blind Cyclops in his cavern;” when searching for the light of truth he too frequently wandered from its shrine.

(5.) It does not appear that the physical phenomena of Light ever received much attention from the ancient philosophers. In their first attempts to explain vision, they gave to the eye a power of projecting material rays, by which the forms and visible qualities of bodies were *felt out*; but they were at length induced to abandon this absurdity, and adopted the idea of Light as a peculiar medium, through which impressions were made on the eye, but in what manner was left quite undetermined. The heating power of the sun’s rays could not escape notice; and the story of the mirrors of Archimides sufficiently proves that considerable attention had been paid to the laws of reflection.

The task of developing the progress of the science of Optics, is not that to which we have to direct attention. That extraordinary property of the solar beam, by which chemical changes of the most singular kind are brought about, in living and in dead matter, in organic and inorganic bodies, is the sole subject of investigation.

(6.) Although the most ordinary observer must, through all time, have noticed that the sun's rays weakened and even destroyed some colours, while others were darkened by their influence, yet these facts excited no attention; and it was reserved for the philosophers of our own time to show, that the study of this peculiar property of the Sunbeam tends to improve our perceptions of the beautiful, and leads to the discovery of some of the most important truths connected with the secret operations of organisation.

(7.) At an early period the beauty of crystalline gems attracted attention; and, being used, then as now, extensively for the purpose of adorning the person, the search for diamonds, rubies, and sapphires was often a very lucrative employment. As some of these precious stones were said to possess the property of shining in the dark, and as most of them refract the luminous rays with extraordinary brilliancy, it became a matter of conjecture if they shone with their own light, or if it was, that they again poured out light which they had the power of absorbing. Several Italians and others wrote on this subject, amongst whom Boetius de Boot was distinguished by his freedom from the philosophy of the schools; and we find him saying, "No man ever durst aver he had actually seen that stone that of itself afforded light." That eccentric and extraordinary genius Benvenuto Cellini, however, affirms, in his Treatise on Jewellery, that he has seen the *carbuncle glowing like a coal with its own light*. The only advantage gained by this discussion was, that it led some to endeavour to prepare substances which should possess the property of emitting light in the dark; and curiosity was at

length gratified by the discovery of the *Phosphorus hermeticus*, of *Balduinus*, of the *Bolonian Stone*, and several of the phenomena of phosphorescence.

(8.) Amidst all the error and charlatanry of the alchemists, we find many important observations and some really great discoveries. Amongst these empirical philosophers were men gifted with minds of a superior order, and the exceedingly careful experiments made by them, whilst they were endeavouring to torture the base metals into gold, and to distil the Elixir Vitæ, became the guiding lights to modern science. In 1556 it was noticed that horn silver (*chloride of silver fused*) was blackened by the sun's rays. This and other peculiar influences which the alchemists observed, led them to fancy that the "sulphurous principle" of Light was one of the most important agents in giving to Nature her infinite variety of form. Possessed with the idea, borrowed from the ancients, that all matter was compounded of three or four simple elements, many of these experimentalists regarded Light as the great primary cause, which modified their *salt*, *sulphur*, and *mercury*, and transmuted them into the earths and metals, or the myriad forms of organic matter. A notion, indeed, somewhat similar to this prevailed amongst the ancient philosophers, for Democritus speaks of minute atoms in swift motion, which, by their smallness and rapidity, were able to permeate the hardest bodies.

(9.) "The sun's rays," Homberg at a much later period says, "will insinuate themselves into bodies so as greatly to increase their weight;" and he seriously relates that four ounces of *Regulus Martis*, in powder, were augmented by  $\frac{1}{10}$  in the balance, by being exposed for an hour at the distance of a foot and a half from the focus of the Duke of Orleans' burning-glass, notwithstanding much of it was dissipated in smoke: the absorption of oxygen was, of course, unknown to the ingenious Homberg. It will be interesting to review a few more of his assertions connected with this part of the subject. "A perfect metal," he writes, "is

nothing but very pure mercury, whose small particles are every way pierced and filled with the sulphureous principle, or the matter of Light, which links and binds the whole mass together." "Gold differs from silver in nothing but in having the globules of the mercury, whereof it consists, penetrated through and through, and being more fully saturated with the sulphureous principle of the rays of Light." "The Light of the sun," he continues, "impinging against terrestrial bodies, modifies them according to their several textures; the luminous matter insinuates itself into the substance of bodies, to produce their sulphur, changes the arrangement of their parts; increases them, and consequently alters the substance of the body itself, after as many different manners as in different quantities it can be differently placed. So that, would we compare the variety of the materials which exist with those which might be brought into being, by all the combinations possible to be made, we must say that the universe, so far as we know of it, is but very small in comparison of what it might be; and that if there were several worlds, formed like this of ours, they might all be differently furnished with objects, without changing either the manner or the matter of the bodies whereof they should consist; which demonstrates an infinite contrivance and power in the Being who made the universe."\*

(10.) Amidst the incorrect views of Homberg, the result of working with one idea, there continually breaks forth a fine philosophy; and we find the illustrious Newton entertaining a similar view to that just quoted, but he lends to the speculation all that refinement which distinguishes every effort of his master mind. Sir Isaac Newton demands, whether "gross bodies and Light are not convertible into one another; and may not bodies receive much of their activity from the particles of Light which enter into their composition? For all fixed bodies, being

\* French Memoirs, from 1700 to 1705.

heated, emit Light so long as they remain sufficiently heated; and Light mutually stops in bodies as often as its rays strike upon their parts."

The hypothesis of Homberg, and the question of Newton, both exhibit striking proofs of remarkable penetration, and afford evidence of minds struggling to burst through the materialities which empiricism had crowded around the science of their times. The hypothesis of the alchymist has been exalted into a probable theory by the discoveries of the modern chemist: and when we reflect that the question asked by Newton remains still unanswered, we should restrain the railroad speed of the science of our day, gliding as it does too commonly over the easiest paths, and viewing in its rapid transit the surface of nature merely.

(11.) I cannot quit this part of my subject without referring to some of the speculations of the talented, though credulous Boyle. I do this, not with any idea of supporting his views, which I regard as being, to a certain extent, visionary, but for the purpose of showing, that long before inductive science had proved the chemical agencies of the different rays of the prismatic spectrum, the curiosity of a gifted mind had advanced very nearly to the truth. In the "Memoirs for a General History of the Air," we find the following remarkable passages, which, although to a certain extent an apology for astrology, are full of suggestions; and, to use Boyle's own words, "wholly to neglect the physical use of the motion of these bodies (the planets), because superstition has crept in, is very extravagant, and ought not to pass uncensured in men of learning."

"Thus every planet," Boyle writes, "has its own proper Light distinct from that of the others, which is either a bare quality, and then its utmost use and design is only to illuminate, or else all Light is attended with some peculiar power, virtue, or tincture; whence 'tis plain that every Light has its peculiar property, tincture, and colour — its own specific virtue and power, wherein the planets differ

from each other ; and consequently the celestial bodies are not to be considered as sluggish and unorganised matter, but as full of their proper motion, operation, and life. Thus the sun not only shines upon all the planets, but by his genial warmth calls forth, excites, and raises the motions, properties, and powers peculiar to them : whence, according to the angle they make with that grand luminary, and the degree wherein they are enlightened, either by its direct or oblique rays, in a near or remote situation in respect of the earth, must be more or less perceived by us. As for the manner wherein the planets transmit their powers, and thereby affect the remote bodies, 'tis not difficult to apprehend it ; for we affirm no virtue or power to flow from the planets that comes not along with the Light as a property thereof." The correctness of the following has been strikingly confirmed by the researches of Faraday on magnetic force, and the investigations of Sabine on the phenomena of terrestrial magnetism.

"As the other planets, so also our earth, is not only enlightened, warmed, cherished, and made fruitful by the power, virtue, and influence of the sun, but it hath, moreover, its proper, magnetical, planetary force awakened, fermented, excited, and agitated, which it sends back with the reflected Light of that luminary."\*

In the same Memoirs, Boyle notices the Oriental tradition, that the rays of the moon produce a baleful effect upon persons exposed asleep to their influence. I may here remark that the popular notion of timber trees being materially influenced by the Light of the moon appears, from a very early period, to have been a generally-received idea ; and the Honduras mahogany trees are cut by the natives at a particular period of the moon's age.

(12.) Notwithstanding that many of those remarkable phenomena which were supposed to be dependent upon some peculiar principle of Light were curiously observed,

\* Boyle's Works, vol. iii. p. 39.

it does not appear that experimental evidence of any value was obtained. A large amount of curious facts was collected—effects depending on very diversified causes were recorded, all of which were attributed to that *element* which the author was inclined to regard as the most important and active in his scheme of creation, to the rejection of every other power.

(13.) A more correct record of observations now opens before us. In 1722 Petit showed that solutions of salt-petre (nitrate of potash) and sal-ammoniac (hydro-chloride of ammonia) crystallised more readily in the Light than they did in darkness.\* These experiments continued, for some time, to excite considerable attention; and in 1788 we find the “vegetation of salts the subject of Chaptal’s inquiry†, and in the following year M. Dizé published a paper upon the crystallisation of salts by the action of Light.

(14.) Charles William Scheele of Stralsund, in Swedish Pomerania, one of the most brilliant geniuses of his or of any age, was the first who analysed the action, and studied the influences, of the differently-coloured rays of Light.‡ The investigations of this chemist are so complete of their kind, and so little known, that I shall give a general view of his experiments. I am induced to this more particularly from the circumstance that much discussion has arisen on a subject,—the change which takes place in the salts of silver employed in Photography,—carefully settled by Scheele in 1777, although his object was to prove that the inflammable principle “*phlogiston*” existed in Light.

“It is well known,” says Scheele, “that the solution of silver in acid of nitre (*nitrate of silver*), poured on a piece

\* Sur la Végétation des Sels. Mém. de Paris, 1722.

† Observations sur l’Influence de l’Air et de la Lumière dans la Végétation des Sels. Mémoires de l’Acad. Royale des Sciences de Toulouse, vol. iii.

‡ Scheele, Traité de l’Air et du Feu.



of chalk, and exposed to the beams of the sun, grows black. The Light of the sun reflected from a white wall has the same effect, though more slowly. Heat without Light has no effect on the mixture. Should the black colour not be real silver ?” “I put some silver earth (*oxide of silver*) on a piece of porcelain, and exposed it in the focus of a burning glass ; immediately the surface of this earth was reduced to silver.”

The following experiments are instructive.

“I precipitated a solution of silver by sal-ammoniac ; then I edulcorated and dried the precipitate, and exposed it to the beams of the sun for the space of two weeks, when the surface of the white paper grew black ; after which I stirred the powder and repeated the same several times. Hereupon I poured some caustic spirit of sal-ammoniac (strong ammonia) on this, in all appearance, black powder, and set it by for digestion. This menstrum dissolved a quantity of *luna cornua* (horn silver), though some black powder remained undissolved. The powder having been washed, was, for the greater part, dissolved by a pure acid of nitre, which, by the operation, acquired volatility. This solution I precipitated again by means of sal-ammoniac into horn silver. Hence it follows that the blackness which the *luna cornua* acquires from the sun’s Light, and likewise the solution of silver poured on chalk, is *silver by reduction*.”

“I mixed so much of distilled water with well edulcorated horn silver as would just cover this powder. The half of this mixture I poured into a white crystal phial, exposed it to the beams of the sun, and shook it several times each day ; the other half I set by in a dark place. After having exposed the one mixture during the space of two weeks, I filtrated the water standing over the *luna cornua* grown already black ; I let some of this water fall by drops in a solution of silver, which was immediately precipitated into horn silver.”

Scheele continued his experiments on the chloride of gold, and some of the salts of manganese, obtaining similar results.

Again, Scheele writes, "Fix a glass prism at the window, and let the refracted sunbeams fall on the floor; in this coloured light put a paper strewed with luna cornua, and you will observe that this horn silver grows sooner black in the violet ray than in any of the other rays, *i. e.* that the calx of silver separates the phlogiston sooner from the violet ray of light than from any other colour."

This is the first intimation we have of the dissimilar action of the refracted rays — the interpretation given was of course discarded with the theory of phlogiston; but the fact observed, has led the way to the discovery of all the phenomena which depend on the chemical agency of the solar rays.

Senebier, who repeated the experiments of Scheele, states that he found the violet ray to darken the chloride of silver in fifteen minutes, while the red rays required twenty minutes, and the other colours various intermediate periods.\* The bleaching of wax by exposure to the solar rays became also the subject of Senebier's investigations.

It became about this time, the latter part of the eighteenth century, a question whether the observed chemical changes were produced by the Light, properly so called, of the solar rays, or by the heat which accompanied it.

(15.) Count Rumford, in a Memoir "*On the Propagation of Heat in Fluids*," published in the Philosophical Transactions, states, that he saw reason to doubt the existence of those chemical properties in Light which had been attributed to it; and, to conclude, that all those visible changes produced in bodies by the action of the sun's rays were effected merely by the *heat* which is generated or excited by the Light which is absorbed by them. In 1798 this philosopher communicated to the Royal Society a Paper, entitled "*An Inquiry concerning the Chemical Properties that have been attributed to Light*." The experimental in-

\* Senebier sur la Lumière, tom. iii. p. 199.

vestigations recorded in this memoir are important, as marking the progress of the inquiry.

Count Rumford found that gold and silver might be melted by the heat—invisible to sight—which exists in the air at the distance of more than an inch above the point of the flame of a wax candle. He then proceeded to examine what would be the effect of this heat on the oxides of these metals. Having wetted a piece of taffeta riband with a saturated solution of the chloride of gold, it was held, stretched horizontally, over the clear bright flame of a wax candle, the under side of the riband being kept at the distance of about an inch and a half above the point of the flame: that part of the riband which was directly over the point of the flame began almost immediately to emit steam in dense clouds; and, in about ten seconds, a circular spot, about three quarters of an inch in diameter, having become nearly dry, a spot of a very fine purple colour, approaching to crimson, suddenly made its appearance in the middle of it, and, spreading rapidly on all sides, became, in one or two seconds more, nearly an inch in diameter. The hue was not uniform, but varied from a light crimson to a very deep purple, approaching to a reddish brown. No traces of revived gold could be discovered, but the riband had all the appearance of being covered with a thin coating of the most beautiful purple enamel, which, in the sun, had a degree of brilliancy that was sometimes quite dazzling.

Whatever material was saturated with the solution of gold, the same stain was produced by the agency of a strong heat; and it was found that solutions of silver, under similar circumstances, imparted stains of a deep orange colour. It was ascertained by several trials that the *light* of a candle produced no change, the decomposition of the salts of gold and silver in these experiments being solely effected by the agency of *heat*.

(16.) Count Rumford next proceeded to examine what influence was exerted by the direct solar rays. Pieces of

riband were wetted, and parcels of magnesia moistened with a solution of gold: those which were exposed to the strong Light of the sun gradually changed colour, and in a few hours acquired a fine purple hue, whilst those preserved in darkness remained unchanged. It was also found, that the decomposition was more readily brought about, when the riband or the magnesia were exposed in a damp state, than if the solution was permitted to dry on them previous to exposure.

(17.) Arguing from the facility with which most of the metallic oxides are reduced, by means of charcoal when exposed to a high temperature, that gold might be revived from its solutions in the same manner, if the solution and the charcoal were equally exposed to a sufficient degree of heat, Count Rumford instituted some experiments to put this idea to the test. He found, by putting small pieces of charcoal into a glass tube filled with solutions of gold or of silver, and exposing it to a temperature of  $210^{\circ}$  Fahrenheit for two hours in the dark, that revived gold adhered to the surface of the charcoal. Similar tubes filled with solution of gold or of silver and fragments of charcoal were exposed to the direct rays of a very bright sun, and in less than half an hour small specks of revived gold in all its metallic splendour, appeared on the surface of the charcoal. Etherial solutions of gold were found to be decomposed by the solar rays, and even by prolonged exposure to diffused Light. Spirits of turpentine and olive-oil were mixed with aqueous solutions of gold and silver, and exposed to heat in a steam apparatus: both of them assisted in reviving the metals, but spirits of wine had no such influence, notwithstanding the presence of carbon, which enters nearly as largely into its composition as it does into the composition of the other two. From these results Count Rumford concludes, that heat is generated by the absorption of the sun's rays; that at the moment of its generation it exists in almost infinitely small spaces; and consequently it is only in bodies that are inconceivably

small that it can produce durable effects, in any degree indicative of its extreme intensity. Mr. Robert Harrup appears to have investigated this subject with much care, and he determined the fact, that several of the salts of mercury were reduced by the Light, and not by the heat of the sun's rays.\*

(18.) In 1775 B. C. Méese first published some experiments upon the influence of Light on plants; and in 1779 Dr. Priestley gave his experiments on the same subjects to the world. There are few examples in the records of science in England, which exhibit more perfectly the advantages of the inductive system than those well-conducted experiments by Priestley. He determined the problem of vegetable respiration—he showed, that carbonic acid was absorbed by the plant, that under the influence of Light it was decomposed, and that its oxygen was again liberated.† Upon the publication of Priestley's researches, a great number of naturalists and chemists took up the inquiry, and many important facts, all of them confirming Priestley's discoveries, were published by Senebier, Ingenhousz, Decandolle, Saussure, and Ritter.‡

(19.) The general result of the investigations on the chemistry of vegetation, up to this point, was, that Light was essential to healthful vegetation; but that the decomposition of the carbonic acid by the plant took place

\* Nicholson's Journal, August, 1804.

† Priestley, *Experiments and Observations on different Kinds of Air, and other branches of Natural Philosophy*. Printed at Birmingham, 1790.

‡ Senebier, *Expériences sur l'Action de la Lumière Solaire dans la Végétation*. Paris, 1788.

Ingenhousz, *Expériences sur les Végétaux*. Philosophical Transactions, 1782.

Decandolle, *Mémoires des Savans Étrangers*, vol. i.

Saussure, *Recherches Chimiques sur la Végétation*. Annales de Chimie, vol. i.

Ritter, *Gehlen Journal der Chem*, vol. vi.

more decidedly under the influence of the most refrangible range of the spectrum, than of those which possessed superior illuminating power. In 1801, Labillardière communicated to the Philomathic Society his discovery that Light was necessary to the development of pores in plants; and about the same time Victor Michellotti, of Turin, published a statement, at that time doubted, but the truth of which has since been confirmed, to the effect "that Light has a decided action on those germs which are exposed to it,—that this action is prejudicial to them, and it manifests its action by retarding their expansion if the Light be weak or a reflected Light, or by total extinction of their life if it be very intense, as that which comes directly from the sun.\* In connection with this section of the inquiry, M. Macaire Prinseps observed, "that sheltering leaves from the action of Light prevents their change of colour in the autumn; that if the entire leaf was placed in the dark it fell off green; if only a part, the rest of the parenchyma changed colour, and the covered portion retained its original colour."† Researches of this character were continued by different investigators, a list of whom is given in a report furnished to the British Association in 1850.

(20.) Böckman found that, by exposing phosphorus in nitrogen and other gases to sunshine, there was deposited upon the side of the glasses nearest the Light a coloured powder, whilst no such effect was produced upon the parts in shadow. He also appears to have observed that the two ends of the solar spectrum produced dissimilar effects on phosphorus.‡

(21.) In 1801, Ritter, of Jena, repeated the experiments of Scheele, and rose the question of the existence

\* Experiments and Observations on the Vitality of Germs. *Journal de Physique Ventose*, p. 9.

† *Mémoires de la Société de Physique et d'Histoire Naturelle de Genève*, tom. iv. p. 1.

‡ Voigt's Magazine, vol. iv.

of solar rays possessing very powerful properties in producing chemical change, which do not act sensibly upon the organs of vision, or which, in other words, are not Light-giving rays. Ritter found that the chloride of silver darkened rapidly *beyond* the violet extremity of the prismatic spectrum; in the violet ray it was less darkened; still less in the blue; below which ray the power of darkening diminished quickly. He also stated that the red ray had the power of restoring darkened chloride of silver to its original colour; and hence concluded that there are two sets of invisible rays, one on the red side of the prismatic spectrum, which favours oxygenation, and the other on the violet side, which assist disoxygenation. The error into which Ritter fell here was only one of degree,—the inequality of action, and the apparently opposite effects produced by the most and by the least refrangible rays has been fully proved. Ritter also states, that he found phosphorus to emit white fumes in the invisible red rays, but that no such effect was produced by the invisible violet rays; this was merely the effect of heat.

(22.) Dr. Wollaston in 1802, examined the chemical action of the rays of the spectrum; and in his Memoir\* he says, "This and other effects usually attributed to Light are not in fact owing to any of the rays usually perceived." About the same period Desmortiers observed that the sun's rays produced a decolouration of Prussian blue; at a somewhat later period Dr. Wollaston showed that cards moistened with tincture of gum guaiacum acquired a green colour in the violet rays, which colour was rapidly destroyed by the red rays. In 1802, M. Sage† noticed that crystals of ruby arsenic effloresced in the Light.

(23.) In the Philosophical Transactions for 1804, Dr. Young gives an interesting experiment, which, although

\* Philosophical Transactions, 1802, p. 379.

† Journal de Physique, 1802.

of a different character, confirms the results obtained by Ritter and Wollaston: "In order to complete the comparison of their properties (the chemical rays) with those of visible Light, I was desirous of examining the effect of their reflection from a thin plate of air, capable of producing the well-known rings of colours. For this purpose I formed an image of the rings, by means of the solar microscope, with the apparatus which I have described in the Journals of the Royal Institution; and I threw this image on paper dipped in a solution of nitrate of silver, placed at the distance of about nine inches from the microscope. In the course of an hour, portions of three *dark rings* were very distinctly visible, much smaller than the brightest rings of the coloured image, and coinciding very nearly, in their dimensions, with the rings of violet Light, that appeared upon the interposition of violet glass. I thought the dark rings were a little smaller than the violet rings, but the difference was not sufficiently great to be accurately ascertained: it might be as much as  $\frac{1}{30}$  or  $\frac{1}{40}$  of the diameters, but not greater. It is the less surprising that the difference should be so small, as the dimensions of the coloured rings do not by any means vary at the violet end of the spectrum so rapidly as at the red end. The experiment in its present state is sufficient to complete the analogy of the invisible with the visible rays, and to show that they are equally liable to the general law, which is the principal subject of this Paper," that is, the interference of Light.

(24.) In 1806, Vogel exposed fat, carefully protected from the influence of the air, to Light, and it became in a short time of a yellow colour: it acquired a rancid penetrating smell and a bitter taste, producing a burning sensation in the throat; whereas that which was open to the air, during exposure, always became acid. The same observer found that ammonia and phosphorus exposed to the sun's rays were rapidly converted into phosphuretted hydrogen and a black powder—phosphuret of ammonia.



Vogel also noticed that the red rays of the prismatic spectrum produced no effect upon a solution of corrosive sublimate (bichloride of mercury) in ether, but that the blue rays rapidly decomposed it.\* He also observed that the decomposition of several metallic compounds was gradually brought on by the same class of rays. Dr. Davy much more recently repeated these experiments, and he found that corrosive sublimate in crystals was not changed by exposure, but that the "liquor hydrargyri oxymur." of the London Pharmacopœia quickly decomposed in sunshine, depositing calomel.

(25.) In the Transactions of the Royal Society of London for 1800, Dr. Herschel's Memoirs on the heating Power of the Solar Spectrum will be found. Previously to this time it was supposed that each ray contributed its proportional share to the intensity of the heat which is produced by the concentration of the sun's rays in the focus of a burning-glass. Dr. Herschel was, however, led to suspect that this was not the fact, from the following circumstances:—"In a variety of experiments," says this philosopher, "which I have occasionally made, relating to the method of viewing the sun with large telescopes to the best advantage, I used various combinations of differently coloured darkening-glasses. What appeared remarkable was, that when I used some of them, I felt a sensation of heat, though I had but little Light; while others gave me much Light, with scarce any sensation of heat. Now, as in these combinations, the sun's image was also differently coloured, it occurred to me that the prismatic rays might have the power of heating bodies very unequally distributed among them." These experiments, having an important bearing on the chemical phenomena which form the principal subject of investigation, will be especially noticed in the next chapter. Herschel also describes his experiments to determine the illuminating powers of the different rays. He discovered that

\* *Annales de Chimie*, vol. lxxv. fig. 225.

the yellow and green rays afforded the greatest quantity of Light, and that the violet ray had the least. In conclusion, Dr. Herschel asks, " May not the chemical properties of the prismatic colours be as different as those which relate to heat and Light ?"

(26.) Seebeck, in 1810, made some important observations on the influences of the solar radiations, the production of *colours on chloride of silver* being among the most remarkable. He tells us the violet rays rendered it *brown*, the blue rays produced a shade of *blue*, the yellow preserved it white, and the red rays constantly gave a red colour to that metallic salt. Berzelius noticed some of the peculiar conditions, described in a future page, in the action of the sun's rays on the salts of gold. Fischer also pursued some researches of a similar character to those of Seebeck, whose results he generally confirmed.\*

(27.) Gay Lussac and Thenard, when engaged on some investigations on chlorine, observed that when mixed with hydrogen it did not combine in the dark ; that they combined slowly in diffused light, and with an explosion in the sunshine. Seebeck collected chlorine over hot water ; and combining it with hydrogen, he placed equal quantities of the mixture in a yellowish red and in a blue glass. In the blue glass, combination took place instantly when the mixture was exposed to daylight, but without explosion. The mixture in the red glass was exposed by twenty minutes without apparent change. When, however, the mixture was transferred from the red vessel to a white one it combined instantly in sunshine, without any explosion. This evidently indicates some physical change, such as we include under the term Allotropism, which will receive attention in its proper section.

(28.) Sir Henry Englefield, at the suggestion of Sir Humphry Davy, tried several experiments with respect to the power of the several coloured rays in rendering

\* Philosophical Magazine, vol. vii. 2 ser. p. 462.

Canton's phosphorus luminous. It was found that the blue rays possessed that power in the highest degree, and there was reason to suspect that this power extended beyond the visible violet ray.

(29.) About this period Dr. Blackburne put forth a theory that Light was a compound of caloric and oxygen; but it does not appear to have found any supporters. In the consideration of the very remarkable phenomena connected with the changes produced by Light, it will be evident that the heat-giving rays, often very materially modify the results; hence the above sketch of the very interesting discoveries of Dr. Herschel will be found to be perfectly in place.

(30.) By far the most important series of researches, however, which were undertaken were those of M. Berard, in 1812, which were examined and reported on by Chaptal, Berthollet, and Biot. In their report they say, "M. Berard found that the chemical intensity was greatest at the violet end of the spectrum, and that it extended, as Ritter and Wollaston had observed, a little beyond that extremity. When he left substances exposed for a certain time to the action of each ray, he observed sensible effects, though with an intensity continually decreasing in the indigo and blue rays. Hence we must consider it as extremely probable, that if he had been able to employ reactions still more sensible he would have observed analogous effects, but still more feeble, even in the other rays. To show clearly the great disproportion which exists in this respect between the energies of different rays, M. Berard concentrated, by means of a lens, all that part of the spectrum which extends from *the green to the extreme violet*; and he concentrated, by means of another lens, all that portion which extends from *the green to the extremity of the red*. This last pencil formed *a white point so brilliant that the eyes were scarcely able to endure it; yet the muriate of silver remained exposed more than two hours to this brilliant point of light, without undergoing any sensible alteration*. On the

other hand, when exposed to the other pencil, which was much less bright and less hot, it was blackened in less than six minutes." This is the earliest intimation we have of any indication that the luminous and chemical powers may be due to dissimilar agencies. On this, the Commissioners remark:—"If we wish to consider solar light as composed of *three distinct substances*, one of which occasions *light*, another *heat*, and the third *chemical combinations*; it will follow that each of these substances is separable by the prism into an infinity of different modifications, like light itself; since we find by experiment, that each of the three properties, *chemical*, *colorific*, and *calorific*, is spread, though unequally, over a certain extent of the spectrum. Hence we must suppose, on that hypothesis, that there exists *three spectrums* one above another; namely a calorific, a colorific, and a chemical spectrum. We must likewise admit that each of the substances which compose the three spectrums, and even each molecule of unequal refrangibility which constitutes these substances, is endowed, like the molecules of visible light, with the property of being polarized by reflection, and of escaping from reflection in the same positions as the luminous molecules, &c." Some other objections to M. Berard's views are then urged.

(31.) Being desirous of including within this general notice, all the phenomena of chemical change which had been observed as being produced by the solar rays, the experiments of Wedgwood and Davy, as belonging especially to photography, have been passed over in the order of time. To a consideration of these, however, it is necessary now to return.

In June, 1802, Mr. Thomas Wedgwood, the son of the celebrated porcelain manufacturer, published, in the Journals of the Royal Institution, "An Account of a Method of Copying Paintings upon Glass, and of making Profiles by the Agency of Light upon Nitrate of Silver; with Observations by H. Davy." This was certainly the first published account of any attempt to produce images by the decom-

posing powers of Light. It does indeed appear, that nearly about the same time M. Charles, in his lectures at Paris, proposed to make use of a prepared paper, to produce black profiles by the action of Light, but he died without disclosing the preparation which he employed; indeed his countryman the Abbé Moigno admits that Charles left "no authentic document to attest his discovery." Mr. Wedgwood made use of white paper, or white leather, moistened with a solution of nitrate of silver. Notwithstanding the imperfect character of his process, it is so very interesting, as the first attempt at producing pictures by Light, that I shall copy the author's description of it, and some of the remarks, from the Memoir:—

(32.) "White paper, or white leather, moistened with solution of nitrate of silver, undergoes no change when kept in a dark place, but on being exposed to the daylight it speedily changes colour, and after passing through different shades of grey and brown, becomes at length nearly black. The alterations of colour take place more speedily in proportion as the Light is more intense. In the direct beams of the sun, two or three minutes are sufficient to produce the full effect; in the shade several hours are required, and Light transmitted through different coloured glasses, acts upon it with different degrees of intensity. Thus it is found that red rays, or the common sunbeams passed through red glass, have very little action upon it; yellow and green are more efficacious, but blue and violet Light produce the most decided and powerful effects.  
 \* \* \* \* \* When the shadow of any figure is thrown upon the prepared surface, the part concealed by it remains white, and the other parts speedily become dark. For copying paintings on glass, the solution should be applied on leather, and in this case it is more readily acted on than when paper is used. After the colour has been once fixed on the leather or paper, it cannot be removed by the application of water, or water and soap, and it is

in a high degree permanent. The copy of a painting or the profile, immediately after being taken, must be kept in an obscure place; it may, indeed, be examined in the shade, but in this case the exposure should be only for a few minutes; by the Light of candles or lamps, as commonly employed, it is not sensibly affected. No attempts that have been made to prevent the uncoloured parts of the copy or profile from being acted upon by Light have as yet been successful. They have been covered with a thin coating of fine varnish, but this has not destroyed their susceptibility of becoming coloured; and even after repeated washings, sufficient of the active part of the saline matter will still adhere to the white parts of the leather or paper, to cause them to become dark when exposed to the rays of the sun. Besides the applications of this method of copying that have just been mentioned, there are many others; and it will be useful for making delineations of all such objects as are possessed of a texture partly opaque and partly transparent. The woody fibres of leaves and the wings of insects may be pretty accurately represented by means of it; and in this case it is only necessary to cause the direct solar Light to pass through them, and to receive the shadows upon prepared leather. \* \* \* \* \* The images formed by means of a camera obscura have been found to be too faint to produce, in any moderate time, an effect upon the nitrate of silver. To copy these images was the first object of Mr. Wedgwood, in his researches on the subject; and for this purpose he first used the nitrate of silver, which was mentioned to him by a friend, as a substance very sensible to the influence of Light, but all his numerous experiments as to their primary end proved unsuccessful. In following these processes, I have found that the images of small objects, produced by means of the solar microscope, may be copied without difficulty on prepared paper. This will probably be a useful application of the method; that it may be employed successfully, however, it is necessary

that the paper be placed at but a small distance from the lens. (*Davy*.) \* \* \* In comparing the effects produced by Light upon muriate of silver with those produced upon the nitrate, it seemed evident that the muriate was the most susceptible, and both were more readily acted upon when moist than when dry, a fact long ago known. Even in the twilight, the colour of moist muriate of silver, spread upon paper, slowly changed from white to faint violet; though, under similar circumstances, no immediate alteration was produced upon the nitrate. \* \* \* \* \* Nothing but a method of preventing the unshaded parts of the delineation from being coloured by exposure to the day, is wanting to render this process as useful as it is elegant."

The failure of two such eminent men as Wedgwood and Davy, in their attempts to produce Light-drawn pictures, appears to have discouraged any further experiments of this kind at that time in England. It must not, however, be forgotten that their progress in this path was stopped only by the want of a solvent for the chloride of silver, which chemical science had not furnished at that time. Had the hyposulphite of soda been known to Wedgwood, the full discovery of photography would have been completed by him.

(33.) In 1814, M. Niepce, of Châlons on the Saône, turned his attention to the chemical agency of Light, his object being to fix the images of the camera obscura; and he appears to have discovered the peculiar property of Light in altering the solubility of many resinous substances. In 1824 M. Daguerre began a series of experiments with the same object in view. The first substances used by him were, according to M. Arago, paper impregnated with a solution of the nitrate or chloride of silver, but his ill success induced him to abandon them. It is not, however, clear whether any other substances or materials were used by Daguerre previously to 1826, when, through a Parisian optician, he became acquainted with

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M. Niepce. In 1827 M. Niepce was in England, and in the December of that year he communicated\* an account of his experiments to the Royal Society of London, together with several pictures on metal plates, some of them in the state of advanced etchings, the etching being effected by acid, subsequent to that part of the process in

\* Through the kindness of Professor Wheatstone, I am enabled to add the following letters, written to Mr. Bauer, which will serve to show the progress made by M. Niepce at this date:—

## No. 1.

Monsieur,

Kew, le 19<sup>me</sup> Novembre, 1827.

Lorsque j'ai quitté la France pour me rendre ici, je m'occupais de recherches *sur la manière de fixer l'image des objets par l'action de la lumière*. J'avais obtenu quelques résultats que je me suis empressé de faire venir. Je desirerais qu'il pût vous être agréable de les voir. Votre suffrage, Monsieur, si toute fois j'en étais digne, me flatterait infiniment, et je me féliciterais d'avoir fait naître une circonstance qui devait me procurer l'honneur de vous connaître.

NICÉPHORE NIEPCE.

## No. 2.

Monsieur,

Kew, le 22<sup>me</sup> Novembre, 1827.

J'ai l'honneur de vous adresser une petite notice sur les recherches qui m'occupent. Elle n'aura pas l'inconvénient de fatiguer par sa longueur; mais je ne sais si elle remplira bien son objet. Il m'eût été pourtant difficile de m'expliquer d'une manière satisfaisante sur certains détails, sans compromettre mon secret. J'ai donc dû me borner à quelques considérations relatives aux perfectionnemens que réclament mes timides essais aux yeux de la critique, même la plus indulgente. Si cependant, Monsieur, vous en jugiez autrement, j'ose compter assez sur votre bienveillant intérêt pour vous prier de me faire connaître votre opinion à cet égard, et je m'y conformerai. Je désire vivement que ma découverte mérite de fixer l'attention de la Société Royale, et que dans ce cas, sa décision ne me soit pas défavorable, parceque alors je n'éprouverais probablement plus de difficulté pour faire parvenir mon hommage au pied du trône. C'est sous ce double rapport, Monsieur, que la recommandation et l'appui d'une person aussi influente que M. le Vice-Président de la Société, me seraient infiniment utiles. Vous voudrez donc bien me permettre de me rappeler aussi là-dessus à votre obligeant souvenir. Nous nous proposons d'avoir l'honneur de vous voir après demain, si toute fois notre visite ne vous dérange pas.

NICÉPHORE NIEPCE. ●



which Light assisted in laying bare portions of the resin-covered plate. These early productions prove, that the

## No. 3.

Monsieur,

Kew, le 30<sup>me</sup> Novembre, 1827.

Je m'empresse de vous faire passer plus tôt que plus tard mes essais de dessin et de gravure d'après mes procédés *héliographiques*. Veuillez avoir la complaisance de me faire prévenir de l'arrivée de M. votre collègue; je serais, on ne peut plus, flatté de le voir, et de m'entretenir quelques instans avec lui. Mon intention ainsi que j'ai eu l'honneur de vous le dire hier, relativement à la présentation de mes essais, est simplement d'obtenir de la Société Royale un avis qui ne soit pas défavorable au résultat de ma démarche subséquente. Je pense, Monsieur, que cette démarche, c'est à dire, l'hommage de ma découverte à sa Majesté Britannique, ne m'empêcherait pas de m'adresser ensuite à la Société des Arts: je la désirerais puisque c'est là principalement où je pourrais trouver toutes les ressources qui me seraient nécessaires pour perfectionner et utiliser l'objet de mes recherches: je suis, en effet, bien décidé, dans ce cas, à leur donner suite ici plutôt qu'ailleurs. Pardonnez, je vous prie, mon importunité; elle a peut-être son excuse dans l'intérêt même que vous avez bien voulu de m'accorder.

NICÉPHORE NIEPCE.

## No. 4.

Monsieur,

Kew, le 28<sup>me</sup> Décembre, 1827.

En réfléchissant à l'obligeante attention que vous avez eu tout récemment, de faire donner communication de ma notice à Mr. le docteur Wollaston, et à un autre savant distingué, j'éprouve un vif regret de ne l'avoir pas su plutôt; mais les bonnes inspirations ne viennent jamais trop tard, lorsqu'il y a encore possibilité d'en profiter. Je désirerais donc savoir si, par votre médiation, Monsieur, je pourrais espérer d'obtenir une lettre de recommandation qui me mît en rapport avec ces savans. Je verrais du moins, dans le véritable intérêt qu'ils portent à la science, le gage certain de celui qu'ils pourraient prendre à ma découverte; et ce résultat seul, serait déjà quelque chose de très-flatteur pour moi. Mais peut-être seraient-ils eux-mêmes à portée de me procurer la connaissance de quelques unes de ces personnes vouées par goût au culte des arts, et plus dans le cas, par leur grande fortune, de les protéger utilement, que des artistes voués presque exclusivement à un autre culte. Cette réflexion, Monsieur, me ramène à la démarche qu'on vient de me faire faire, et dont je ne puis que fort mal augurer. Aussi serais-je charmé que vous voulussiez bien consentir à celle que j'ai l'honneur de vous proposer. Je me féliciterais d'autant plus qu'elle réussit, que je me plais à la regarder comme une heureuse inspiration du constant intérêt que vous avez daigné m'ac-

experimentalist of Châlons was acquainted with the method of making the shadows and lights of his pictures

corder jusqu'ici. Veuillez ne pas prendre la peine de m'écrire ; mais faites-moi dire seulement de passer chez vous, Monsieur, si vous le désirez, et je m'empresserai de m'y rendre. J'attends, au premier jour, une réponse décisive de Mr. Watkins ; et en cas qu'elle ne soit pas satisfaisante, ainsi que j'ai lieu de le presumer, je m'occuperais de suite de la nouvelle démarche, qui serait très-probablement la dernière.

N. NIEPCE.

No. 5.

Le 17<sup>me</sup> Janvier, 1828.

J'ai écrit hier à Mr. le Docteur Wollaston : j'attends de réponse ce soir.

No. 6.

Châlons-sur-Saône, le 10<sup>me</sup> Mars, 1828.

[Refers wholly to private matters.] Nous sommes arrivés ici le 26<sup>me</sup> Février.

No. 7.

Châlons-sur-Saône, le 4<sup>me</sup> Mai, 1828.

J'ai pris, durant notre séjour prolongé à Paris, mes mesures de précaution en me procurant tout ce qui pouvait m'être nécessaire pour la continuation de mon travail. J'ai fait construire par l'opticien Vincent-Chevalier, un objectif achromatique qui donnera infailliblement dans la chambre noire, plus de champ et plus de netteté aux images représentées. Il m'a confectionné pareillement, pour le même objet, une verre périscope d'après le système de Dr. Wollaston. Je serai ainsi à portée de comparer et de juger lequel des deux procédés est le plus avantageux. Je n'ai pas négligé de voir M. Lemaître, graveur, et M. Daguerre : j'ai eu avec eux plusieurs entrevues, et ils m'ont bien recommandé de profiter de la belle saison pour donner suite à mes recherches. M. Lemaître m'a dit obligeamment, que je pouvais disposer de son burin ; il m'a même prié de lui envoyer quelques points de vue d'après nature, préparés sur cuivre, et il se chargera de les graver. J'ai reçu aussi de M. Daguerre beaucoup de témoignage d'obligeance, et surtout d'excellens conseils que je tâcherai de mettre à profit. Depuis mon retour ici, je n'ai plus eu de rapport avec eux ; je ne me propose même de leur écrire que lorsque j'aurai obtenu un résultat décisif, si toute fois je puis m'en flatter. Quant à M. Daguerre, je ne sais d'ailleurs où le trouver ; car il se disposait à faire quelques courses, ou plutôt quelques voyages, ce qui me porte à croire qu'il n'est pas à Paris dans ce moment. Quoique les nouveaux appareils auxquels je fais travailler ici ne soient pas encore dispo-

correspond with those of nature, and of rendering his copies impervious to the erasing effects of the solar rays.

nibles, ça ne m'a point empêché, Monsieur, de reprendre mes expériences héliographiques d'après les moyens de perfectionnement indiqués dans ma notice. Je suis même déjà dans le cas de reconnaître que je ne m'étais point trompé dans l'appréciation de quelques-uns de ces moyens appliqués, je ne dis pas à la gravure, mais au dessin d'objets vus dans la chambre noire. En parlant de ces dernières données, j'ai lieu de bien augurer de mes prochains essais de points de vue d'après nature, quoique ce genre de représentation soit sans doute ce qu'il y a de plus difficile, et que je ne prétende pas arriver ainsi d'emblée à la perfection. Voici le moment le plus favorable : la campagne est revêtue de tout l'éclat de sa parure ; j'attends donc avec impatience que mes appareils soient prêt pour me mettre en mesure d'opérer. Si j'obtiens d'heureux résultats, j'aurai, Monsieur, le plaisir de vous en instruire, et de répondre même par là, j'en suis sûr, au vif intérêt que vous voulez bien prendre à l'objet de mes recherches. Dans ce cas, vous me permettrez aussi, je l'espère, de vous offrir celui de mes nouveaux essais qu'on aura jugé plus de vous être présenté ; mais n'anticipons pas sur l'avenir : il y a souvent à celui du mécompte, et je sens que je me laisse trop entraîner par une illusion à laquelle la reconnaissance prête encore plus de charme.

N. NIEPCE.

#### No. 8.

Monsieur,

Châlons-sur-Saône, le 9<sup>me</sup> Janvier, 1829.

En continuant, comme je vous l'annonçais, mes recherches héliographiques, j'espérais toujours parvenir à un résultat décisif et digne, sous ce rapport, de vous être présenté. Cet espoir ne s'est point entièrement réalisé. Je dirai toute fois, avec la même franchise, que je suis aujourd'hui beaucoup plus rapproché du but qu'il me tarde d'atteindre. Vous vous rappelez peut-être, Monsieur, les moyens de perfectionnement indiqués dans ma *notice*. Je n'ai pas négligé d'en faire l'application ; et j'en augure trop bien jusqu'ici pour ne pas m'en occuper de nouveau, dès que le retour de la belle saison me permettra de reprendre mon travail. J'ai aussi reconnu, d'après quelques essais sur la verre, la possibilité d'imiter avec la plus grande vérité, et tout le prestige d'illusion, les effets du *diorama*, sauf pourtant la magic du coloris. Mais, Monsieur, autant je doutais, dans le principe, qu'il fût possible de représenter les objets avec leurs couleurs naturelles, comme je serais disposé à le croire maintenant. L'expérience m'a procuré là-dessus des données qui viendraient jusqu'à un certain point à l'appui de cette conjecture, et seraient en même tems une conséquence assez directe de la théorie de Newton sur les anneaux colorés. Malgré cela, il y aurait

(34.) In a paper dated the 5th December, 1829, M. Niepce communicated to M. Daguerre the particulars of

plus que de la témérité de ma part à donner à quelques résultats prématurés une importance qu'ils sont encore loin de mériter; et si j'ose vous les communiquer, Monsieur, avec tout l'abandon de la confiance, c'est pour ne rien vous laisser ignorer de ce qui se rattache à des recherches auxquelles vous voulez bien prendre un si vif et si constant intérêt. Dans quelques mois d'ici je les poursuivrai, je l'espère, avec de nouvelles garanties de succès, pourvu que la saison me soit moins défavorable que l'an passé; et je me bornerai d'abord à une seule application de mes procédés, à fin d'arriver plus promptement au but. Si j'ai ce bonheur là, Monsieur, vous pouvez compter sur mon empressement à vous le faire savoir.

N. NIEPCE.

No. 9.

Monsieur,

Paris, 3<sup>me</sup> Février, 1828.

Depuis votre départ j'ai fait deux tableaux, un pour le Diorama, et l'autre pour l'exposition du musée, ce qui m'a occupé toute l'espace du tems, ce qui fait que je n'ai pu donner aucune suite à mes recherches.

Quant à vous, Monsieur, je vois avec peine que vos occupations vous ont détournées de votre intéressante découverte, et que vous n'avez trouvé en quelque sort que découragement en Angleterre. Mais, consolez-vous: il n'est pas possible qu'il en soit de même ici; surtout, si vous arrivez au résultat que vous avez droit d'espérer, je puis vous assurer qu'on ne verra pas cela avec la même indifférence. Je me ferai un véritable plaisir, si cela peut vous être agréable, de vous indiquer les moyens d'en tirer de meilleure partie. Je ne puis vous dissimuler que je brûle du désir de voir vos essais d'après nature; car si ma découverte a pour base un principe plus incompréhensible, il n'en est pas moins que vous êtes bien plus avancé dans les résultats, ce qui doit nécessairement vous encourager.

DAGUERRE.

M. NIEPCE.

Specimens of Heliography given by M. Niepce to the late Francis Bauer, Esq., of Kew, and now in the possession of Dr. Robert Brown, of the British Museum.

1. A design  $5\frac{1}{2}$  by 4 inches longways, on a pewter plate  $6\frac{1}{2}$  by  $5\frac{1}{2}$  inches; it is stated at the back to have been taken from a print about  $2\frac{1}{2}$  feet long. The picture represents the ruins of an abbey: in a proper light it is very distinct.

the process employed by him, and they entered into an agreement to pursue, for their mutual benefit, the researches which they had respectively begun. As many parts of this process of M. Niepce's, and some of his remarks, are curious and interesting, I shall devote a brief space to a few extracts from this communication :\*—

“The discovery which I have made,” says M. Niepce, “and to which I give the name of Heliography, consists in producing spontaneously, by the action of Light, with gradations of tints from black to white, the images received by the camera obscura.

“Light, in its state of composition and decomposition, acts chemically upon bodies. It is absorbed, it combines with them, and communicates to them new properties. Thus it augments the natural consistency of

2. A view  $7\frac{1}{2}$  inches by 6 inches longways, on a pewter plate 8 by  $6\frac{1}{2}$  inches ; it is stated on the back to have been N. Niepce's first successful experiment of fixing permanently the image from nature. The view is of a court-yard seen from an upper window. It is less distinct than the former ; the outlines of the black portions are bordered by a white fringe, whiter than the adjacent parts. The surfaces on which the pictures appear are metallic, but are blacker, and reflect more light than the under pewter surfaces ; the colour appears to be that of lead or platinum. No. 1. has experienced no injury. No. 2. is covered in some parts with minute brown spots.

3. A design  $4\frac{1}{2}$  by  $5\frac{1}{2}$  inches upright, on a pewter plate 8 by  $5\frac{1}{2}$  inches, from a print, the subject “Christ bearing the Cross :” every line is beautifully distinct.

4. A copy from a print of a head  $6\frac{1}{2}$  by  $5\frac{1}{2}$  inches, upright, on a plate 7 by  $5\frac{1}{2}$  inches, etched by an after process, with two extremely good impressions of the plate.

5. An impression from a plate 8 by  $7\frac{1}{2}$  inches : the design is a landscape and ruin,  $6\frac{3}{4}$  by  $4\frac{1}{2}$  longways. The lines are beautifully distinct in parts.

Besides the above, M. Niepce presented a beautiful specimen to Mr. Cassells of Richmond, the subject of which appears to be the same as No. 5. It is also understood that M. Niepce presented some plates to the late Sir Everard Home.

\* See History and Practice of Photogenic Drawing, by M. Daguerre, translated from the original by T. S. Memez, LL.D. London, 1839.

some of these bodies : it solidifies them even, and renders them more or less insoluble, according to the duration or intensity of its action.

“ The substance which has succeeded best with me, and which concurs most immediately to produce the effect, is asphaltum or bitumen of Judea, prepared in the following manner:—I about half fill a wine-glass with this pulverised bitumen. I pour upon it, drop by drop, the essential oil of lavender, till the bitumen can absorb no more. I afterwards add as much more of the essential oil, as will cause the whole to stand about three lines above the mixture, which is then covered and submitted to a gentle heat, until the essential oil is fully impregnated with the colouring matter of the bitumen. If this varnish is not of the required consistency, it is to be allowed to evaporate slowly, without heat, in a shallow dish, care being taken to protect it from moisture, by which it is injured, and at last decomposed. A tablet of plated silver is to be highly polished, on which a thin coating of the varnish is to be applied cold, with a light roll of very soft skin ; this will impart to it a fine vermilion colour, and cover it with a very thin and equal coating. The plate is then placed upon heated iron, which is wrapped round with several folds of paper, from which, by this method, all moisture has been previously expelled. When the varnish has ceased to simmer, the plate is withdrawn from the heat, and left to cool and dry in a gentle temperature, and protected from a damp atmosphere.

“ The plate thus prepared may be immediately submitted to the action of the luminous fluid, in the focus of the camera. But even, after having been thus exposed a length of time sufficient for receiving the impressions of external objects, nothing is apparent to show that these impressions exist. The forms of the future picture remain still invisible. The next operation then is to disengage the shrouded imagery, and this is accomplished by a solvent.”

This solvent consists of a mixture of one part, by volume, of the essential oil of lavender, and ten of oil of white petroleum. A vessel being procured of a sufficient size, enough of this solvent to cover the plate is poured in. "Into this liquid the tablet is plunged, and the operator, observing it by reflected Light, begins to perceive the images of the objects to which it had been exposed gradually unfolding their forms, though still veiled by the supernatant fluid, continually becoming darker from saturation with varnish. The plate is then lifted out, and held in a vertical position till as much as possible of the solvent has been allowed to drop away." The pictured tablet is now carefully washed by being placed upon an inclined plane, over which a stream of water is carefully poured.

It should be observed that the Light solidifies the varnish, and renders it less soluble than the parts upon which the shadows have fallen. In the same communication M. Niepce says, "It were, however, to be desired that, by blackening the plate, we could obtain all the gradations of tones from black to white; I have therefore turned my attention to this subject, and employed at first liquid sulphate of potash (sulphuret of potassium?). But when concentrated it attacks the varnish; and if reduced with water, it only reddens the metal. This twofold defect obliged me to give it up. The substance which I now employ is *iodine, which possesses the property of evaporating at the ordinary temperatures.*" It will be seen that the Daguerreotype process, which derives its name from its discoverer, consists in the application of iodine to silver plates, which is decomposed by the influence of Light.

(35.) It appears probable, that the discovery of the Daguerreotype was owing to some observations of Daguerre's, on the changes produced by Light on those silvered plates covered with films of iodine. M. Daguerre, however, appears to imply the contrary, in a note which

however, appears to imply the contrary, in a note which he has appended to M. Niepce's paper. This heliographic process was exceedingly tedious and uncertain. An exposure of two or three hours was necessary to produce an impression from an engraving, even under the influence of a bright sun; and in the camera obscura, the plate was left under the influence of strong Light for six or eight hours, and sometimes even longer, before a tolerable picture could be produced. M. Daguerre materially modified and improved this process. The resin of the essential oil of lavender, dissolved in alcohol, was found by him to be more susceptible of change than the bitumen; and instead of washing the plate with the solvent recommended by M. Niepce, which often removed all the varnish from it, he exposed the tablet to the vapour of petroleum, by which a much more certain effect was produced.

(36.) A correspondence between M. Niepce and M. Daguerre has been published, which sufficiently proves, that to the latter the sole merit of the discovery of the process which bears his name is due. In 1831-2, M. Niepce indeed regrets that, at the recommendation of M. Daguerre, he had lost so much time in experiments on iodine. "I repeat it, Sir," he says, "I do not see that we can hope to derive any advantage from this process, more than from any other method which depends upon the use of metallic oxides," &c. &c. In another letter he speaks of a decoction of thlapsi\* (shepherd's purse), fumes of phosphorus, and particularly of sulphur, as acting on silver in the same way as iodine, and that caloric produced the same effect by oxidising the metal, "*for from this cause proceeded in all these instances this extreme sensibility to light.*" We may perceive, from these remarks, that although M. Niepce may not have been fortunate enough to discover the exquisitely sensitive method of M. Daguerre, he must have submitted to experiment a great variety of substances

\* Thlapsi Bursa-pastoris (Linn.), Capsélla Bursa-P. (De Candole.)



in different states of combination. The philosopher of Châlons died in July, 1833, and a new agreement was entered into between his son, M. Isidore Niepce, and Daguerre.

(37.) In January, 1839, the discovery of M. Daguerre was reported, and specimens shown to the scientific world of Paris. The extreme fidelity, the beautiful gradations of light and shadow, the minuteness, and the extraordinary character of these pictured tablets, took all by surprise. Europe and the New World were alike astonished at the fact, that Light could be made to delineate on solid bodies, delicately beautiful pictures, geometrically true, of those objects which it illuminated. In the July following, after a bill was passed, securing to M. Daguerre a pension for life of 6000 francs, and to M. Isidore Niepce of 4000 francs, with one half in reversion to their widows, the process by which these pictures were produced was published.

(38.) Mr. Henry Fox Talbot informs us that in 1834 he began some experiments with a view of rendering the images of the camera obscura permanent. On the 31st of January, 1839, six months prior to the publication of M. Daguerre's process, a paper giving an account of Mr. Talbot's labours, entitled, "Some Account of the Art of Photogenic Drawing, or the Process by which Natural Objects may be made to delineate themselves without the aid of the Artist's Pencil," was read before the Royal Society; and in another communication on the 21st of February, 1839, the method of preparing the paper was given, and the process by which the design was fixed described. In these, however, there will be found but little advance upon the process of Mr. Wedgwood: the mode of fixing, which was the only novelty proposed by Mr. Talbot, was imperfect; the process of fixing by the use of the hyposulphite of soda belonging to Sir J. Herschel and Daguerre.

(39.) It will be evident to all, that the researches of the French artist and of the English philosopher were pursued,

without any knowledge of each other's labours. The results in both cases were satisfactory, and they equally rendered most important service; to Science, in producing an instrument by which some of the mysterious phenomena of Light could be investigated, and to Art, by giving its votaries tablets, upon which Nature impresses herself in all her delicacy and decision, in all her softness and her grandeur, and in all her richness of tone and breadth of effect. Colour alone is wanting, and there are sufficient reasons for believing, that in the progress of research, we shall, before long, arrive at processes, by which the delightful pictures of the camera obscura shall be rendered permanent in all the beauty of those glowing tints, which give to the fields of creation their exquisite charm and enchanting character.

## CHAPTER II.

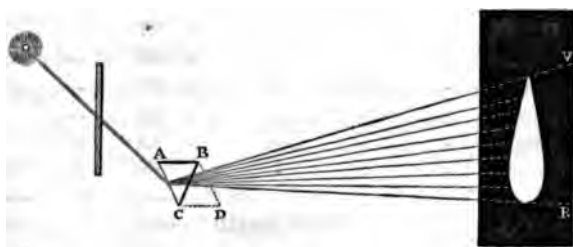
## ANALYSIS OF THE SUNBEAM.

(40.) It is important on entering on the study of a set of phenomena, which are still among the novelties of science, that we should make ourselves acquainted with all the conditions, which may directly or indirectly influence them. The chemical changes produced by the solar rays have usually been regarded as a function of Light (the *luminous principle* as distinguished from heat or any other power). It has been stated in the historical chapter (30) that some of the Continental philosophers, and particularly Berard, were disposed to refer the phenomena of chemical change under the influence of radiant action, to some principle which, although associated with Light in the sunbeam, as heat is, was still to be distinguished from Light, by its being incapable of producing *visibility*, or *colour*. The object of this volume being the full examination of this problem, it is proposed to consider the phenomena of the strictly *luminous radiations*, and of the *heat radiations*, previously to entering on the investigation of the chemistry of the sunbeam.

(41.) If a hole is made in the window-shutter of a darkened room, there will be, if the sun is shining, a bright circular image formed upon the floor, or on a screen placed to receive it. This circular spot of Light is an image of the sun, as we may prove by placing the eye, protected by a smoked glass, in the path of the sunbeam, when that luminary will be distinctly seen through the hole, or, if we receive such an image when the sun is partially eclipsed, it will exhibit only the still luminous portion of the disc.

(42.) If in the path of the beam we interpose a prism

of glass, as A B C in the accompanying figure, having one of its angles downwards, and so adjusted to the incident sunbeam, that it falls obliquely on one of its sides, A C, the pencil of light will be turned out of its path or *refracted*. The luminous image will now be thrown upwards, and, instead of forming a circular white spot, it will be elongated into a flame-like image, consisting of several beautifully coloured bands, R V. This image is called a *spectrum*; we speak of it as a solar or a prismatic spectrum, and it is sometimes termed the Newtonian spectrum, since the first satisfactory examination of the solar beam by prismatic decomposition was performed by Sir Isaac Newton.



(43.) Sir Isaac Newton, in 1666, published the results of his researches. He determined the number of rays, into which white Light was decomposed by the prism, as seven, and that the respective length of each ray was relatively as indicated in the following table. I have placed by the side of Newton's measurements the results of Frannhofer's more recent examination, with far more perfect instruments than any which Newton could command. The differences are in many respects striking, but since under any circumstances these measurements must depend upon the power of the eye of the observer to distinguish accurately the line between two colours fading one into the other, it is scarcely possible that any two observers should give the same limits to any particular coloured ray. I have frequently tried the experiment of desiring different people to mark with a needle the commencement and termination

of the red ray, and it has scarcely ever happened that any two have indicated the same limits. Some eyes are far more sensitive to some particular colours than others are; and as some people can hear sounds which are inaudible to others, so colour is detected by some eyes, over spaces, from which other eyes receive no chromatic impression. The determination of the dark lines in the spectrum, to be presently noticed, has greatly facilitated the measurement of the rays, but still the objection urged remains in all its force.

(44.) *Newton and Frannhofer's measurement of the rays of the spectrum :—*

1. Red	-	-	-	-	45	—	56
2. Orange	-	-	-	-	27	—	27
3. Yellow	-	-	-	-	40	—	27
4. Green	-	-	-	-	60	—	46
5. Blue	-	-	-	-	60	—	48
6. Indigo	-	-	-	-	48	—	47
7. Violet	-	-	-	-	80	—	109
				Total length	360		360

(45.) Sir Isaac Newton showed, that the different rays of Light had different indices of refraction; the index of refraction for *red* light being the least, and that of the *violet* the largest, in the spectrum then known. His celebrated doctrine of *the different refrangibility of the rays of light* is given in a series of propositions, of which the two first will serve our purpose:

“1. As the rays of light differ in degrees of refrangibility, so they also differ in their disposition to exhibit this or that particular colour. Colours are not qualifications of Light, derived from refractions or reflections of natural bodies, but original and connate properties, which in divers rays are divers,” &c.

“2. To the same degree of refrangibility ever belongs the same colour, and to the same colour ever belongs the same degree of refrangibility. The least refrangible rays

are all disposed to exhibit a red colour, and contrarily, those rays which are disposed to exhibit a red colour are all the least refrangible; so the most refrangible rays are all disposed to exhibit a deep violet, and contrarily, those which are apt to exhibit such a violet colour are all the most refrangible; and so to all the intermediate colours, in a continued series, belong intermediate degrees of refrangibility. And this analogy between colours and refrangibility is very precise and strict; the rays always agreeing exactly in both, or proportionally disagreeing in both."\*

(46.) Sir Isaac Newton having, by his investigations, established the composition of white Light by analysis, proceeded to prove this by synthesis. We obtain this proof in the following manner:—If the screen upon which the spectrum is received is brought nearer the prism, the rays begin to mix; yet, even when brought close to the prism, the colours are evident. If another prism  $BCD$ , as shown by the dotted lines in the former figure, made of the same kind of glass, is placed with its angles in an opposite direction to the first prism, the coloured rays are again combined, and a white spot as before falls upon the floor.

(47.) It has been repeatedly stated that the union of the coloured rays into white Light may be illustrated by mixing together seven different powders, corresponding in colour and proportions with the prismatic rays. Such an union is said to produce a *greyish white*, and this falling short is attributed to the inferiority of all artificially prepared colours. The fact is, however, that no such result as that stated can be obtained. However careful we may be as to the proportions in which the powders are mixed, and in selecting those of the utmost purity, a dull neutral tint approaching to *black*, and not to white, will be ob-

\* Newton's Optics.

tained. The rotation of a disc coloured to correspond with the spectral rays, does give rise to a *grey white*. Not because the rays from those surfaces blend into white, but because they pass the eye so rapidly, that no one of them has time to fix its impression on the retina before it is obliterated by the next in order.

(48.) Sir David Brewster instituted an examination of the compound nature of Light by absorption; that is by viewing the spectrum after the rays have been subjected to the absorptive action of different colour media. That my readers may be in a position to value the reasonings of Sir David Brewster, I shall rapidly analyse his experiments and observations.

1. Simple inspection of the spectrum proves that red Light exists in the red, orange, and violet rays; that is, that according to the measurements of Frannhofer 192 parts out of the 360 give direct evidence of red Light.

2. The eye detects yellow Light in the orange, yellow, and green, and these rays occupy 100 parts of the spectrum.

3. Blue Light is seen to exist in the violet, indigo, blue and green spaces, therefore occupying 250 parts out of the 360.

(49.) (a.) If the blue and indigo rays are examined through a certain thickness of olive oil, they acquire a perceptible violet tint; proving the existence of *red* in the blue and indigo, as well as in the *violet* rays.

(b.) Seen through a certain thickness of balsam of sulphur, the red rays show a green band; these are considered necessarily, therefore, as containing *blue and yellow*.

(c.) White Light in all parts of the spectrum may be proved: when the spectrum is viewed through a considerable thickness of blue glass it displays only a yellow colour, and if the thickness is increased it becomes a greenish white. A solution of sulphate of copper and red ink produces the same effect.

Proceeding in this manner we are enabled to trace *red*,

*yellow, blue, and also white* Light over every part of the spectrum.

(50.) “*Difference of colour,*” says this philosopher, “*is therefore not a test of difference of refrangibility,* and the conclusion deduced by Newton is no longer admissible as a general truth.” For a full examination of this question I must refer to the original papers.\* The following are this author’s general conclusions:—

1. *Red, yellow, and blue* exist at every point of the solar spectrum.

2. As certain portions of *red, yellow, and blue* constitute white Light, the colour of every point of the spectrum may be considered as consisting of the predominating colour at any point mixed with white Light. In the red spaces there is more red than is necessary to make white Light with the small portions of yellow and blue which exist there; in the yellow space there is more yellow than is necessary to make white Light with the red and blue; and in that part of the blue space which appears violet there is more red than yellow; and hence, the excess of red forms a violet with the blue.

3. By absorbing the excess of any colour at any point of the spectrum above what is necessary to form white Light, we may actually cause white Light to appear at that point, and this white Light will possess the remarkable property of remaining white after any number of refractions, and of being decomposable only by absorption.

(51.) Slight consideration will show that these views suppose these coloured bands to be composed of three primary spectra of equal lengths,—a red, a yellow, and a blue spectrum overlapping each other, and exhibiting the colours of the Newtonian spectrum by allowing one to be seen through that one which overlaps it.

(52.) M. Bernard of Bordeaux has shown,—1st, That

\* Transactions of the Royal Society of Edinburgh, vol. xii. ; and “A Treatise on Optics,” by Sir David Brewster. Edin. 1853.



the intensity of the Light has such influence on the sensation of colour, that it may not only modify the aspect of the entire spectrum, but certain tints may disappear altogether. 2nd, That the absorption produced by the action of media hitherto employed on the tints of the spectrum, only affects the intensity of the light, and does not influence the nature of the colours; and 3rd, That far from destroying the bond which appears to exist between refrangibility and colouration, observations made with care tend to confirm the opposite opinion; every thing, indeed, leads to the belief that to each ray of a given refrangibility, and possessing a determined intensity, corresponds a colour susceptible of being reproduced, identically under like circumstances.

(53.) M. Helmholtz has recently subjected the spectrum to a searching analysis; and the result is opposed to the views of Brewster, while they confirm those of Newton.\* M. Helmholtz is disposed to refer the phenomena observed by Brewster, when viewing the spectrum through differently coloured media, to a diffusion of the light of the adjoining rays, over the particular ray under examination; and he supposes this to arise from extra refraction in the prism and in the transparent coloured lamina employed, by dust, striæ, and the like producing secondary images. Helmholtz has adopted the following arrangement, to make the experiment in such a manner as to avoid all influence of diffusion. A solar spectrum is produced in the usual way, by means of a prism, and a lens placed at a suitable distance from a narrow slit admitting the solar rays. The screen which receives the spectrum is itself perforated by a slit, which can be adjusted at will to any colour; in this way is insulated a very slender luminous pencil of any of

\* On the Theory of Compound Colours. Poggendorff's *Annales*, 1852. *Phil. Mag.* 1854, vol. iv.

On Sir David Brewster's New Analysis of Light. *Ibid.* *Phil. Mag.* *ibid.*

the rays under examination, which are rendered thus perfectly homogeneous. This pencil is received on a second prism, to which succeeds a lens: the group of homogeneous rays throws upon a suitably adjusted screen a narrow image of the slip. It will be evident that by such an arrangement as this, a pencil of light may be obtained which will be *pure*, the very trifling quantity of diffused light by which it may be accompanied being too feeble to be taken into account. The results obtained by this method support the Newtonian law of the strict relation of colour to the refracting angle. For example, pure yellow seen through blue glass of any thickness whatsoever, always preserves its yellow tint, never passing into white.

(54.) Such is the state of the discussion as to the constitution of the spectrum. Whether the theory of the seven prismatic rays of Newton are to be adopted, or the three supposed spectra of Brewster, it is evident it must undergo much modification to meet the requirements of our more advanced knowledge. Sir John Herschel has shown us, that by looking at the spectrum with a cobalt-blue glass, we perceive a ray, called by him the "*extreme red*," of a crimson colour, below the ordinary red ray of the spectrum.\* Again, by throwing the spectrum upon paper stained yellow by turmeric, a ray of high refrangibility beyond the violet becomes visible, which ray is of a peculiar neutral colour, and has been termed a *grey* or *lavender* ray. Thus the researches of Herschel increase the number of chromatic bands to nine.

(55.) The peculiarity exhibited by a solution of sulphate of quinine in water, acidulated with sulphuric acid, had often excited attention. The solution is transparent and colourless, when we look through it; but when looking

\* See Article Light, Encyclopedia Metropolitana, and On the Chemical Action of the Rays of the Solar Spectrum. Philosophical Transactions, Part I. for 1840.

at it, the light of day falling directly upon the surface observed, it assumes a beautiful silvery blue colour. A green variety of fluor spar exhibits the same phenomenon. It is also strikingly shown by a weak decoction of the inner bark of the horse-chestnut tree, and by some other substances. A peculiar yellow glass, coloured by oxide of uranium, possesses like properties, but the light from it in this case is a pale sea green.

(56.) Sir John Herschel called attention to these phenomena, in two papers published in the *Philosophical Transactions*.\* He showed that the colours came only from a stratum of fluid of small but finite thickness at the surface, by which the light entered. He also proved that a ray of light, having once passed through such a stratum, had lost the power of producing the same effect. This peculiar dispersion of light taking place at or near the surface of the body, was called by Sir John Herschel *Epipolic*; and a beam of light which, after having passed through a solution of quinine, was incapable of again producing the effect, he termed *Epipolised* light.

(57.) Sir David Brewster, in a paper read before the Royal Society of Edinburgh, in 1846†, drew attention to similar phenomena in a solution of the green colouring matter of leaves. These experiments were made by passing a beam of solar light, concentrated by a lens, into the solution or substance under observation. Upon examining the quinine solution in this way, it was found that light was dispersed, not merely close to the surface, but at a long distance within the fluid. These phenomena have been most thoroughly investigated by Mr. Stokes of Cambridge, to whose results attention must now be given.

(58.) Without attempting any description of the numer-

\* On a Case of Superficial Colour, presented by a Homogeneous Liquid internally colourless, and On the Epipolic Dispersion of Light. *Phil. Trans.* 1845.

† On the Decomposition and Dispersion of Light within Solid and Fluid Bodies.

ous and beautiful experiments made by Mr. Stokes and described in his *Memoirs*\*, which is not indeed necessary, I shall give a short account merely of the methods by which these phenomena of dispersion may be viewed, and copy Mr. Stokes' general conclusions.

If a ray of light concentrated by a lens is passed into a solution of sulphate of quinine, or a block of uranium glass, a cone of rays of a blue or a green colour, according as the first or the last is employed, will be seen penetrating the medium, these rays presenting an appearance essentially different from the rays of the ordinary spectrum.

If a pencil of light is refracted by a prism, and these refracted rays being first received on a good achromatic lens, the spectrum is thrown upon either of the above media, or any of those formerly mentioned, and we look through the sides in upon the image, we shall see all the least refrangible rays, rendered evident by moats in the fluid passing freely through; and if the spectrum is received on a screen, but little loss of light or colour will be perceived. From a certain point near the least refrangible violet rays—but this varies somewhat with the medium employed—small cones of light, of the peculiar colours of the light from the surface of the quinine solution, or the canary yellow (uranium) glass, will be seen passing into the solution or glass to various depths, and these will be found to extend with varying degrees of intensity beyond the violet and lavender rays. By this method it is shown that rays of high refrangibility, existing over the space usually included in the term of "Ritter's dark rays," are rendered visible. Hence, it has been inferred that, since the most active chemical rays exist within the limits comprehended by these rays, that they are rendered visible. This question will be discussed in a future section, after a full examination of the chemistry of the solar radiations.

\* On the Change of Refrangibility of Light. By G. Stokes, M. A., F. R. S. *Philosophical Transactions*, 1852.

Mr. Stokes has proposed the term *Fluorescence* to distinguish this peculiar optical phenomenon, since it exists in a marked manner in some varieties of fluor spar.

(59.) The results of his investigations, as given by Mr. Stokes, are the following:—

“ 1. In the phenomena of true internal dispersion, the refrangibility of Light is changed, incident Light of definite refrangibility giving rise to dispersed Light of various refrangibilities.

“ 2. The refrangibility of the incident Light is a superior limit to the refrangibility of the component parts of the dispersed Light.

“ 3. The colour of Light is in general changed by internal dispersion, the new colour always corresponding to the new refrangibility. It is a matter of perfect indifference whether the incident rays belong to the visible or the invisible part of the spectrum.

“ 4. The nature and intensity of Light dispersed by a solution appear to be strictly independent of the state of polarisation of the incident rays. Moreover, whether the incident rays be polarised or unpolarised, the dispersed Light offers no traces of polarisation. It seems to emanate equally in all directions, as if the fluid were self-luminous.

“ 5. The phenomena of a change of refrangibility prove to be extremely common, especially in the case of organic substances, such as those ordinarily met with, in which it is almost always manifested to a greater or less degree.

“ 6. It affords peculiar facilities for the study of the invisible rays of the spectrum, more refrangible than the violet, and of the absorbing action of media with respect to them.

“ 7. It furnishes a new chemical test of a remarkably searching character, which seems likely to prove of great value in the separation of organic compounds. The test is specially remarkable for this, that it leads to the independent recognition of one or more sensitive substances in a mixture of various compounds, and shows to a great ex-

tent, before such substances have been isolated, in what menstrua they are soluble, and with what agents they enter into combination. Unfortunately, these observations require, for the most part, sunlight.

"8. The phenomena of internal dispersion oppose fresh difficulties to the supposition of *a difference of nature in luminous, chemical, phosphorogenic rays, but are perfectly conformable to the supposition that the production of Light, of chemical changes, and of phosphoric excitement, are merely different effects of the same cause.* The phosphorogenic rays of an electric spark, which, as is already known, are interrupted by glass, appear to be nothing more than invisible rays of excessively high refrangibility, which there is no reason for supposing to be of a different nature from the rays of Light."

(60.) The discovery of three or more new sets of rays, the extreme red, the lavender, and the fluorescent rays, still further involves the question of there being three primary rays, or a greater number. An extended series of experiments are still required to determine if it is possible by any means to decompose a ray of definite refrangibility and of pure colour into rays of another colour, or develop physical conditions of a new order, by new systems of refraction, reflection, absorption, or transmission.

(61.) It is essential that the condition of the prismatic image should be distinctly understood; I therefore return to the consideration. The sunbeam, passing through a hole into a darkened room, produces the sun's image on the floor, howsoever small or large that hole may be. If we interpose a prism we produce a spectrum by the refraction of the rays. If we isolate any ray, say the red ray, we find we have a red circular image of the sun; if the blue, we shall obtain a blue circular image, and so on; therefore the spectrum must be regarded as an assemblage of images of different refrangibilities superposed on, and overlapping each other. The more we diminish the

angular diameter of the sun, the less will these prismatic images overlap, and consequently the purer will be the rays of the spectrum we shall obtain; but it will be evident that it is scarcely possible to obtain a spectrum in which we have not some error arising from this cause. In our future examination of the heating powers, and more particularly of the chemical action of the solar beam, the importance of attending to the existence of these conditions will be apparent, and the best arrangement for obtaining a pure spectrum described.

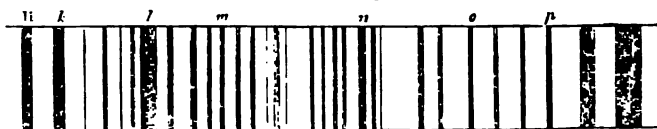
(62.) Howsoever pure the spectrum may be, it is not an uninterrupted line of light, but it is crossed by spaces giving no light—*absolutely dark lines*. These were first noticed by Dr. Wollaston\*; but they were fully examined by Fraunhofer, who, by the aid of his excellent instruments, discovered that the surface of the spectrum was crossed by these dark bands, or, as he terms them, “fixed lines,” of which he observed upwards of 500, although in his drawing of the spectrum he inserted only 354. Sir David Brewster has been enabled to extend the number so largely as to comprehend 2000 lines in a spectrum which he delineated.

Seven of these lines, B, C, D, E, F, G, H, from their distinctness, are particularly distinguished. These are represented in the figure in the Frontispiece. B lies near the outer end of the *red* space; C beyond the middle of the *red*; D in the *orange*, and is a strong double line; E is in the *green*; F in the *blue*; G in the *indigo*; and H in the *violet*. Besides these, there are other lines, which from their decision require notice. At A is a well defined dark line, near the least refrangible edge of the red ray; half way between A and B is a group of seven lines, forming a black band; between B and C are nine lines, and *b* is a triple line in the green; between F and G are 185 lines, and between G and H are 190 of these dark spaces.

\* Philosophical Transactions, 1802.

These lines extend also over those parts which, until Mr. Stokes's inquiry, gave us no evidence of any luminous effect. By forming a spectrum on a Daguerreotype plate, M. E. Becquerel discovered the same lines in the chemical impression, and similar ones formed over the parts acted upon by the obscure rays. A very broad line is formed at *i*, by the union of many smaller lines. After it, at *m* *r*, four other lines are formed; and at *n*, four others. There are at *o* two great lines; and another at *r*, which is very strong and black. A great number of others are formed, and many of them represented in the plate attached to M. E. Becquerel's memoir; but I have not thought it necessary to represent them. It is upon the strength of the fact of the existence of these inactive spaces in the "chemical," as well as in the "luminous," spectrum, that Becquerel inclines to regard the chemical and luminous rays as identical.

(63.) Although the first edition of this Work was published in 1844, and then contained the Frontispiece which is affixed to this edition, in which is copied the fixed lines in the spectrum, as published by Becquerel in 1842\*, it is curious to find Mr. Stokes adding a note, during the printing of his paper, to the effect that, until he forwarded it to the Royal Society, he was unacquainted with Becquerel's Map. "The only map of the fixed lines of the chemical spectrum, which I had for a good while after these researches were commenced, is Professor Draper's."† Mr. Stokes's lines, determined with all the accuracy of his new methods of observation, are shown in the following woodcut. Of these Mr. Stokes says, in his note:—"M. Bec-



querel's broad band *i* is my *l*; his group of four lines *m*

\* *Bibliothèque Universelle de Genève.*

† *Philosophical Magazine*, 1843.



with the preceding band, forms my *m*; his group of four lines *N*, forms the first of my group *n*; his line *o* is my *n*. It is only in the last group that there can be any doubt as to the identification; but I feel almost certain that M. Becquerel's *P* is my *o*; and the next two lines, the last in his map, are the two between *o* and *p*. It is difficult at first to believe that the strong line *p* should have been left out, while the two faint lines between *o* and *p* are represented; but the difficulty is, I think, removed by considering the feeble photographic action in that part of the spectrum."

These fixed lines are so uniform that they are employed with the highest advantage in marking the spaces of the spectrum, instead of referring as formerly to the uncertain appreciation of the chromatic bands.

The bright lines in the spectra of different flames, require no attention in this treatise, although they are phenomena of a highly remarkable character. The longitudinal lines observed by Zantedeschi have not yet been determined with the required accuracy; this reference to them will therefore be sufficient.

(64.) Fraunhofer has given the world the first numerical estimate, on which any real dependence can be placed, of the illuminating power of the solar spectrum. He places the maximum at his line *M*, calling this 100; the Light at other parts being as follows:—

Light at red end	-	0·0	Light at <i>E</i>	-	-	48· 0
— <i>B</i>	-	3·2	— <i>F</i>	-	-	17· 0
— <i>C</i>	-	9·4	— <i>G</i>	-	-	3· 1
— <i>D</i>	-	64·0	— <i>H</i>	-	-	0·56
Maximum at <i>M</i>	-	100·0	Violet extremity	-	-	0·00*

(65.) The experiments made by Dr. Herschel to determine the heating powers of the rays, consisted in passing each ray through an opening in a piece of pasteboard, and placing delicate thermometers with blackened

\* I cannot but express my doubts here, being quite disposed to believe the violet rays to have more illuminating power than the indigo.

balls, so that they could be irradiated with each particular colour. The result of these investigations proved, in the first place, that the red rays possessed a greater amount of heating power than any other of the prismatic coloured rays; and, secondly, led to the discovery of "rays coming from the sun, which are less refrangible than any of those that affect the sight," and which have vested amongst them the maximum of the heating power.

"A beam of radiant heat, emanating from the sun," says Dr. Herschel, "consists of rays that are differently refrangible. The range of their extent, when dispersed by a prism, begins at violet-coloured Light, where they are most refracted, and have the least efficacy. We have traced these calorific rays throughout the whole extent of the prismatic spectrum, and found their power increasing, while their refrangibility was lessened, as far as to the confines of red-coloured Light. But their diminishing refrangibility and increasing power did not stop here; for we have pursued them a considerable way beyond the prismatic spectrum into an invisible state, still exerting their increasing energy, with a decrease of refrangibility, up to the maximum of their power; and have also traced them to that state where, though still less refracted, their energy, on account, we may suppose, of their now failing density, decreased pretty fast; after which, the invisible *thermometrical spectrum*, if I may so call it, soon vanished."

Dr. Herschel determined that the invisible rays exerted a considerable heating power, at a point  $1\frac{1}{2}$  inch distant from the extreme red ray, even though the thermometer was placed at a distance of 52 inches from the prism.

(66.) These experiments were repeated by Sir Henry Englefield, with additional precautions against any source of error, and he found that the thermometer rose in the following order:—

In the blue rays in 3' from  $55^{\circ}$  to  $56^{\circ}$ , or  $1^{\circ}$ .

Green in 3' from  $54^{\circ}$  to  $58^{\circ}$ , or  $4^{\circ}$

Yellow in 3' from  $56^{\circ}$  to  $62^{\circ}$ , or  $6^{\circ}$ .

Full red in  $2\frac{1}{2}'$  from  $56^\circ$  to  $72^\circ$  or  $16^\circ$ .

Confines of the red in  $2\frac{1}{2}'$  from  $58^\circ$  to  $73\frac{1}{2}^\circ$ , or  $15\frac{1}{2}^\circ$ .

Quite out of visible Light in  $2\frac{1}{2}'$  from  $61^\circ$  to  $79^\circ$  or  $18^\circ$ .

(67.) M. Berard obtained similar results, excepting that he placed the maximum of heat at the very extremity of the red rays, instead of beyond them. These experiments were afterwards repeated by Sir Humphry Davy at Geneva, who confirmed the correctness of Dr. Herschel's experiments; and still more recently by M. Seebeck, who has shown that the place of maximum heat varies with the substance of which the prism is made. Seebeck was assisted in his experiments by M. Wunsch; and they came to the following conclusions:—

Substance of the Prism.				Colour of Space in which the Heat is greatest.
Water	-	-	-	Yellow.
Alcohol	-	-	-	Yellow.
Oil of Turpentine	-	-	-	Yellow.
Sulphuric Acid	-	-	-	Orange.
Solution of Muriate of Ammonia	-	-	-	Orange.
Solution of Corrosive Sublimate	-	-	-	Orange.
Crown Glass	-	-	-	Middle of the red.
Plate Glass	-	-	-	Middle of the red.
Flint Glass	-	-	-	Beyond the red.

(68.) Herschel having shown that the largest quantity of solar heat was manifested in the least refrangible rays, and particularly in rays which were not visible to us; and also having proved that the maximum of luminous power was found in the yellow ray—Ritter having demonstrated that invisible rays of great refrangibility had a large amount of chemical power, and Seebeck pointed out that this tendency to produce change was confined to these and the blue rays—it was long the custom to consider the prismatic spectrum as divisible into three classes of rays: the red or calorific rays; the yellow or luminous rays; and the blue or chemical rays. In the first place we are bound to regard all the coloured rays as *luminous rays*, but differing in the intensity of their effects. Calorific power is traced through all the luminous rays, and much below them, whereas chemical action extends, independent of Light at the other end of the spectrum.

(69.) A brief notice of Sir John Herschel's experiments on the thermic spectrum must here have a place. To procure visible effects of the calorific power of the spectrum, the following method was adopted: — "The thinnest post paper, such as is sold for foreign correspondence, was stretched on a frame. One side of this paper was blackened with Indian ink, or, which is better, smoked in the flame of oil of turpentine, or over a smoky candle, by drawing it often and quickly through the flame, giving it time to cool between each exposure, till it is coated on the under side with a film of deposited black, as nearly uniform as possible. The white side of this paper is exposed to the incident spectrum, properly adjusted, keeping the blackened side hollow to admit air and to avoid rubbing off the black coat. A fiducial dot being made on it, and this brought to coincide with the standard yellow ray, a flat brush, equal in breadth to the paper, dipped in good rectified spirits of wine, is to be passed over the white surface till the paper is completely saturated, which will be indicated by its acquiring a uniform blackness in place of the white it at first exhibited.

"After a few minutes a whitish spot begins to appear considerably below the extreme red end of the luminous spectrum, which increases rapidly in breadth until it equals the breadth of the luminous spectrum, and even somewhat surpasses it; and in length, till it forms a long appendage exterior to the spectrum, and extends more-over within it, up to, and beyond the fiducial yellow. In this state, and just as the general drying of the paper begins by whitening the whole surface to confuse the appearances, a second, sudden, and copious wash of alcohol from above downwards must be applied, without disturbing the spectrum, or in any way shaking the apparatus. The superfluous alcohol will have hardly run off when the phenomena of the thermic spectrum will begin to appear in all their characters, at first faintly, and, as it were, sketched in by a dimness and dulness of the other-

wise shining and reflective surface of the wetted paper ; but this is speedily exchanged for a perfect whiteness, marking by a clear and sharp outline the lateral extent of the calorific rays, and by due gradations of intensity, in a longitudinal direction, their law or scale of distribution both within and without the luminous spectrum."

Supposing, then, that such smoked paper is employed, the thermograph of the spectrum in its most complete state, or rather in that succession of states in which each part comes most characteristically into view, is as is represented in the drawing of this thermic spectrum given in the Frontispiece.

Sir John Herschel details some of the results obtained upon different coloured papers, each of which has its peculiar *scale of action*. The results, however, obtained upon smoked paper, which are the most satisfactory, are thus explained by this able philosopher.

"The most singular and striking phenomenon exhibited in the thermic spectrum thus visibly impressed, is its want of continuity. It obviously consists of several distinct patches, of which  $\alpha$ ,  $\beta$ , are the most continuous and intense, but are less distinctly separated, and of which, when the sun is very strong and clear, it is even difficult to trace the separation. The spot  $\gamma$ , on the other hand, is round and well insulated; it begins to appear on the paper soon after the ovals,  $\alpha$ ,  $\beta$ , are fully formed, and when  $\beta$  has assumed a sharply rounded outline. The first symptom of its appearance is the dulling of the wet and shining surface of the paper, which is speedily followed by the appearance of a small round white speck; this continues to increase rapidly in size and whiteness, and at length assumes a definite and perfectly circular outline, within which the paper is entirely white. By degrees the oval  $\beta$  and this spot join and run together, forming a white streak deeply indented at the point of junction. It is not till this happens that similar symptoms begin to betray the existence of a still more remote heat spot,  $\delta$ . Indeed, it generally requires another wash of alcohol before

this can be fully brought into evidence. It is, however, perfectly unequivocal, though very much feebler, and rather worse defined than  $\gamma$ , with which also it is somewhat better connected than  $\gamma$  with  $\beta$ .

(70.) "Of the existence of a much more remote spot," says Sir John Herschel, "I have hardly a doubt, but it is very difficult to obtain a sight of it." This is the spot  $\epsilon$ , situated at about —58. The very accurate measures taken of this spot on several occasions, leave no doubt of its existence, and of the correctness of the remote position assigned to it in the drawing. The great analogy between this arrangement of the heat spots along the axis of the spectrum, and the absorptive action of nitrous gas on the luminous rays, seem, as Sir John Herschel remarks, to point to a gaseous absorption. "The gaseous media through which the rays have reached their point of action, are the atmospheres of the sun and the earth. The effect of the former is beyond our control, unless we could carry our experiments to such a point of delicacy as to operate separately on rays emanating from the centre and borders of the sun's disc. That of the earth's, although it cannot be eliminated any more than in the case of the sun's, may yet be varied to a considerable extent by experiments made at great elevations and under a vertical sun, and compared with others where the sun is more oblique, the situation lower, and the atmospheric pressure of a temporarily high amount. Should it be found that this cause is in reality concerned in the production of the spots, we should see reason to believe that a large portion of solar heat never reaches the earth's surface, and that what is incident on the summits of lofty mountains differs not only in quantity, but also in *quality*, from what the plains receive."

(71.) Now, these facts render it clear, at least to me, that the calorific rays have an existence independent of the luminous rays of the solar spectrum, and that Heat occupies a larger space than Light in the spectrum. Melloni has shown, by some admirable experiments, that bodies are

not alike transparent to Heat and Light. Black mica, obsidian, and black glass in thin laminæ, although nearly opaque to Light, yet allow a large quantity of radiant heat to pass them, and are called by Melloni, *diathermic*\*; whilst glasses of a green colour, in combination with a layer of water, or a very clear plate of alum, are, on the contrary, called *adiathermic*†, from their being perfectly opaque for heat, notwithstanding Light permeates them freely. These points appear quite sufficient to establish the distinctions of the two solar radiations, Heat and Light; although it may eventually, by the advance of experimental science, be shown that they are but different states of one power, we are justified in adopting the popular notion, and regarding them as distinct principles having a common origin.

(72.) When such a prismatic spectrum as we have been examining, is thrown upon a paper covered with chloride of silver, or any other of those chemical preparations which are susceptible of change under the influence of the sun-beam, it will be found that there is no correspondence between either the illuminating or the heating power of the spectrum and the chemical phenomena which result. The three spectra represented in the Frontispiece, will sufficiently explain the differences in the general results. Light, Heat, and Chemical Power or Actinism, as the agent supposed to produce these phenomena is called, exhibit three very dissimilar scales of action. They neither agree in their maxima nor minima in the spectrum, their refrangibility or their physical characters. To the especial consideration of the chemical phenomena produced by radiant force, the remainder of this volume is devoted. The discussion of the question now suggested, is reserved until the examination of a large number of striking phenomena has been properly instituted.

\* From *διὰ*, through, and *θερμὸς*, warm.

† From a priv. and *διαθερμικὸς*, transcalescent.

## CHAPTER III.

## ACTION OF THE SOLAR RAYS ON PREPARATIONS OF SILVER.

(73.) ALTHOUGH the preparations to which our attention must be directed, are those employed as agents for the production of photographic pictures, my object is not to deal with the manipulatory details of the art of photography, any further than they become necessary to the elucidation of the subject before us. Almost every change in the method of applying the argentiferous preparations to the surfaces employed, gives rise to some peculiarity in the action of the prismatic rays upon them. We, therefore, by examining the effect of different modes of preparing the sensitive surface, discover the cause producing increased delicacy in the combination; and to this extent the practice of photography belongs to this Volume. It is thought desirable to examine the action of the spectrum upon the various salts of silver, principally with a view to determine, with as much exactness as possible, the rationale of the chemical changes which take place, and the chemically active state of the rays of the spectrum, viewed in relation to their refrangibility.

(74.) Oxide of silver, prepared by precipitating it in the dark, from a solution of nitrate of silver, by pure potash is, when applied to paper in a pasty state and dried, of a very dark green colour; if it be exposed for a few hours to good sunshine, it passes into a more decided olive colour than characterises it when first prepared by precipitation from the nitrate of silver, and consequently any covered portions vary in colour from those on which the sun's rays fell. Prolonged exposure to the sun's rays, for a week or more, renders this olive colour very much



lighter, and the covered parts are found to be many times darker, than those on which the solar rays have acted directly. In some instances, where the oxide of silver has been spread on paper, I have noticed a very decided whitening process, after a few days' exposure; this evidently arises from the revival of metallic silver. In some experiments I have succeeded in the height of summer, in obtaining so complete a metallic coating that, by passing the paper through a roller, a coating of white silver was obtained.

(75.) The oxide of silver, dissolved in ammonia, is a valuable photographic fluid. One application to paper of a strong solution, forms a tolerably sensitive surface. The ammonia nitrate of silver, which is much used by photographers, may be regarded as essentially the oxide dissolved in ammonia. The most simple and the best mode of proceeding is that introduced by Dr. Alfred Taylor:—Drop ammonia carefully into a solution of nitrate of silver; a copious precipitate falls; still add ammonia until this is entirely redissolved. The spectrum produced on this preparation, is not essentially different from that obtained on the nitrate of silver.

(76.) NITRATE OF SILVER.—This salt in a state of purity, whether solid or in solution in pure distilled water, does not appear to be sensibly affected by Light; but the presence of the smallest portion of organic matter occasions it to blacken, under weak luminous influence. This property induced Sir John Herschel, in his early photographic experiments, to combine organic matter with the solution of the nitrate of silver, previously to its being applied to paper, and afterwards to introduce into the pores of the paper, salts of silver in combination with the organic acids; but without any remarkable results. The organic combinations have, however, since that time been found of exceeding value in quickening the change of many salts of silver under exposure to sunshine. We have already seen that Count Rumford found the nitrate of

silver in contact with charcoal or an earthy carbonate, was soon reduced to the metallic state, under the action of strong sunshine.

(77.) There are some peculiar effects produced when we place a stick of charcoal in a solution of nitrate of silver, to which I have devoted some attention, and on which I have still a series of experiments in progress. A few facts will, however, prove the peculiar nature of the phenomenon of the revival of silver by carbon.

If a stick of charcoal is placed in a bottle in which is some solution of nitrate of silver, so that one half of the charcoal is in the solution, and the other half above it, there will in a short time appear little spangles of silver upon the upper portion of the charcoal, if it is exposed to diffused Light. In full sunshine the effect is greatly retarded. If the bottle is placed in a dimly illuminated place, there will, in the course of a few weeks, form in the solution around the charcoal, a series of the most delicate thread-like crystallisations of the silver. After these have formed, if the bottle is exposed to sunshine, they are gradually redissolved in the fluid. An examination of the influence of the different rays upon the charcoal in these conditions, appears to indicate a more intense action in the least refrangible rays, than in those of higher refrangibility. An extensive series of experiments is, however, necessary to determine many important points connected with the action of carbon on the salts of silver and gold; and by these we should learn more perfectly the action of organic compounds in general.

(78.) A remarkable analogy between the effects of heat and Light deserves notice, and it is also of some practical importance in the preparation of the papers. If a piece of nitrated paper is placed upon hot iron, or held near a good fire, it will be found that at a heat just below that, at which the paper chars, the salt is decomposed. Where the heat is greatest, the silver is revived; and immediately around it, the paper becomes a deep blue; beyond this a

pretty decided green colour results; and beyond the green, a yellow or a yellow brown stain is made.

(79.) *Prismatic Analysis.* — The first published examination of the effects produced by the spectrum on any considerable variety of chemical preparations, was that of Sir John Herschel, to whom we are greatly indebted for a very large amount of the most valuable information on this branch of the inquiry. I feel it a duty which I owe to this distinguished philosopher, to use his own words in describing the phenomena of spectral actions observed by him, as far as is practical; and to distinguish such from my own experiments and remarks, I shall in every case affix his name.

(80.) In the experiments made by myself on the spectrum, I have allowed the solar rays to pass, either a fine slit formed by two knife edges, or a small round hole. This beam fell upon a prism placed at the proper angle; and the spectrum formed was received upon an achromatic lens, and the preparations under examination placed in the focus of the lens.

The prisms employed were very fine pieces of flint glass, which enabled me to see all the principal fixed lines of the luminous spectrum; a very perfect crown-glass prism; one hollow prism, which was commonly filled with castor-oil; and a quartz prism of superior character manufactured by Mr. Darker.

(81.) Paper washed with the solution of nitrate of silver already mentioned, was placed still damp in the proper position, and in few a minutes a good chemical image resulted. The colour of the impressed spectrum on this paper is, at first, a pale brown, which passes slowly into a deeper shade; that portion corresponding with the blue rays, becoming a blue brown; and under the violet of a peculiar pinky shade, I have sometimes observed a very decided green tint, on the point which corresponds with the least refrangible blue rays. (*Herschel.*) Its limit of action, under the most favourable circumstances, commences very

near the centre of the yellow ray; its maximum appears about the centre of the blue, although the action up to the edge of the violet ray is continued with very little diminution of effect; it extends beyond the violet, but the action of the invisible rays is feeble.

(82.) When the spectrum is made to act on nitrated paper, which has been previously darkened by exposure to to sunshine under a solution of the cupro-sulphate of ammonia, the phenomena are materially different. The photographic spectrum is lengthened out on the red or negative side by a faint but very visible red portion, which extends fully up to the end of the red rays, as seen by the naked eye. The tint of the general spectrum, too, instead of brown is dark gray, passing, however, at its most refracted or positive end into a ruddy brown. (*Herschel.*)

(83.) Photographic Application.—Nitrate of silver, although the most valuable of the salts of that metal to the photographer, as from it most of the other argentine compounds can be prepared, is not of itself sufficiently sensible to Light to render it of much use. It may, however, in some few cases, be advantageously employed. If well sized paper is washed over with a solution of 100 grains of the salt in a fluid ounce of distilled water, and dried at a little distance from a warm fire, we form a paper which, for copying lace-work, feathers, and articles of which a perfect outline merely is required, answers well. By soaking the paper previously to applying the wash of nitrate of silver, in isinglass, parchment size, a solution of gum-arabic, or by rubbing it over with the white of egg, the silver darkens much more readily, and eventually acquires a much deeper colour. A pleasing variety of tints for the pictures, may be produced by varying these organic combinations; and a still more interesting series, by precipitating organic liquids with solutions of lead, applying them in the state of cream on paper, and drying, before the nitrate is applied, as recommended by Sir John Herschel. The influence of lead in exalting the oxidation of the silver

salts under the action of sunshine, will be further described in the section on lead. Pictures formed on the nitrated papers are rendered permanent by simply washing, first, in cold, and afterwards soaking in warm water, free from salt.

(84.) CHLORIDE OF SILVER is obtained by adding a solution of chloride of sodium (*muriate of soda*) to a solution of the nitrate of silver. This salt of silver, whether in its precipitated state, or when fused, by which operation we produce the horn silver of the alchemists, changes its colour to a fine bluish gray, by a very short exposure to the sun's rays, or even by prolonged exposure in diffused Light. If the chloride is combined with a small quantity of the nitrate, the change is much more rapid, and the darkening process goes on to a deep brown, which slowly passes into a fine olive. Eventually, after a few weeks, metallic silver is seen to be revived on the surface of the paper. It is somewhat remarkable, that great differences are observed in the colour produced on chlorides of silver precipitate by different muriates. Nearly every variety in combination with the nitrate, becomes *at last* of the same olive colour; it must therefore be understood that the following notices apply to the colour produced by an exposure of a few minutes only to good sunshine, and it must also be recollected that the chloride of silver in these cases is contaminated with the precipitant.

(85.) Muriate of ammonia inclines the precipitated chloride of silver to darken to a fine chocolate brown, whilst chloride of calcium (*muriate of lime*) operates to the production of a brick-red colour. Chlorides of potassium and sodium afford a precipitate, which darkens speedily to a pure bark brown; while hydro-chloric (*muriatic*) acid, or aqueous chlorine, does not carry the darkening beyond the lilac to which the *pure* chloride of silver changes by exposure. As far as my experiments have gone, it appears that this difference of colour is owing to the admixture of the earth or alkali used, with the silver salt, and not to the

presence of organic matter, although it does, as in the case of the nitrate, produce similar varieties of colour. The chlorides of barium and strontium have some peculiar *colorific* properties, when in combination with the chloride and other salts of silver, which well deserve particular attention; however, as these peculiarities are more strikingly exhibited in some of the positive photographic processes which will be eventually described, it will be more in place to reserve the description of their effects.

(86.) *Prismatic Analysis.* — The spectrum impressed upon a paper, spread with the chloride of silver, is often very beautifully tinted, the intensity of the colours varying considerably with the salt employed to precipitate the chloride. Papers prepared with the hydro-chlorate of ammonia or the chloride of barium, and then with two successive washes of the nitrate of silver, have given me, when the sunshine has been favourable, a range of colours very nearly corresponding with the natural hues of the prismatic spectrum. Under favourable circumstances the mean red ray leaves a red impression on the paper, which passes into green over the space occupied by the yellow rays. Above this a leaden blue is discovered, and about the mean blue ray, where the action is greatest, it rapidly passes through brown into black, and through the most refrangible rays it gradually declines into a bluish brown, which tint is continued through the invisible rays. At the least refrangible end of the spectrum, the very remarkable phenomenon has been observed,—in the first instance, by Sir John Herschel,—of the extreme red rays exerting a protecting influence, and preserving the paper from that change which it would otherwise undergo, under the influence of the dispersed light which always surrounds the spectrum. Although this is very evident when the spectrum, concentrated by a good achromatic lens, is received on the muriated paper, it is still more strikingly shown, if we receive the spectrum directly from the prism, without

the interposition of the lens. It indeed appears to me, from many experiments made in this manner, that not only the extreme red ray exerts this very peculiar property, but the ordinary red ray, through nearly its whole length. Including this whitened portion, the whole extent of chemical action exerted is "considerably more than double the total length of the ordinary luminous spectrum. (*Herschel.*)

(87.) *Photographic Application.*—It has been already stated, that the chloride of silver was used as a photographic agent by Wedgwood, Davy, and Daguerre, their success however being very limited. This salt became, in the hands of Mr. Fox Talbot, of much importance. As it is to this experimentalist that we are indebted for the first successful application of any chemical preparation on paper, as a tablet on which Light should impress, with unerring fidelity, the objects it rendered visible, it is right that his process should be described in his own words.

"I select," says Mr. Talbot, "in the first place, paper of a good firm quality and smooth surface. I do not know that any answers better than superfine writing-paper. I dip it into a weak solution of common salt and wipe it dry, by which the salt is uniformly distributed throughout its substance. I then spread a solution of nitrate of silver on one surface only, and dry it at a fire. The solution should not be saturated, but six or eight times diluted with water. When dry the paper is fit for use.

"I have found by experiment, that there is a certain proportion between the quantity of salt and that of the solution of silver, which answers best and gives the maximum effect. If the strength of the salt is augmented beyond this point, the effect diminishes, and in certain cases becomes exceedingly small.

"This paper, if properly made, is very useful for all ordinary photographic purposes. For example, nothing can be more perfect than the images it gives of leaves and

flowers, especially with a summer sun: the light passing through the leaves delineates every ramification of their nerves.

"Now, suppose we take a sheet thus prepared, wash it with a *saturated* solution of salt, and then dry it. We shall find (especially if the paper has been kept some weeks before the trial is made) that its sensibility is greatly diminished, and in some cases seems quite extinct. But if it is again washed with a liberal quantity of the solution of silver, it becomes again sensible to Light, and even more so than it was at first. In this way, by alternately washing the paper with salt and silver, and drying it between times, I have succeeded in increasing its sensibility, to the degree that is requisite for receiving the images of the camera obscura.

"In conducting this operation, it will be found that the results are sometimes more and sometimes less satisfactory, in consequence of small and accidental variations in the proportions employed. It happens sometimes that the chloride of silver is disposed to darken of itself, without any exposure to Light: this shows that the attempt to give it sensibility has been carried too far. The object is to *approach* to this condition as near as possible, without *reaching* it, so that the substance may be in a state ready to yield to the slightest extraneous force, such as the feeble impact of the violet rays when much attenuated. Having therefore prepared a number of sheets of paper, with chemical proportions slightly different from one another, let a piece be cut from each, and having been duly marked or numbered, let them be placed side by side in a very weak diffused light for a quarter of an hour. Then if any one of them, as frequently happens, exhibits a marked advantage over its competitors, I select the paper which bears the corresponding number to be placed in the camera obscura."\*

\* London and Edinburgh Philosophical Magazine, March, 1839, vol. xiv. p. 209.



(88.) This variable sensibility of paper, prepared with the same ingredients, differing but very slightly in their proportions, admits of an easy explanation by an experiment. Precipitate upon a clean piece of glass a film of chloride of silver, which is best done in the following manner recommended by Sir John Herschel:—A solution of common salt of extreme dilution, is mixed with nitrate of silver, so dilute as to form a liquid only slightly milky, and into this, at the bottom of a deep vessel, is placed horizontally a glass plate, upon which the chloride is slowly deposited; the liquid being carefully drawn off with a siphon, and the last portions by fibres of hemp. When this is dry, we have a uniform film of the chloride of silver, chemically pure. If we take this plate, and having placed it at a very small inclination, expose it to Light, and drop upon its upper edge a small portion of a solution of nitrate of silver, we shall see, that, as the nitrate solution slowly combines, as it descends, with the chloride, it darkens very unequally; the edges of the descending liquid giving the most rapid indications of sensibility to sunshine. From this we learn that to produce the most sensitive chloridated photographic paper, it is necessary to have an exceedingly slight excess of the nitrate of silver, beyond that which is necessary to effect the entire decomposition of the salt used; but, as I have stated before, this excess is absolutely essential.

(89.) The following are the best proportions, with which my practice has made me acquainted, for producing papers sufficiently sensitive for good pictures by superposition or for *positives* in general:—

Chloride of sodium, fifty grains to one ounce of water; in which solution the paper is washed, and then carefully wiped over with a clean cotton cloth, and dried.

A solution of the nitrate of silver, in the proportions of 120 grains to an ounce of distilled water, is then carefully applied twice over one side of the sheet, drying the sheet between each wash at a little distance from the fire.

(90.) For the less sensitive varieties of this kind of

paper, the silver salt may be used in more economical proportions. Great care is of course required in all photographic manipulation, and the want of attention to the purity of the materials used, their correct proportions by weight and measure, and the absolute cleanness of brushes, cloths, &c. will constantly lead to the most perplexing failures. It may be well to observe in this place, once for all, that the selection of paper for photographic purposes requires to be made with care. The thing to be aimed at is, to obtain as great a transparency as possible, combined with such a thickness as shall ensure perfect opacity in the dark parts of the drawings. It is also to be desired that the sensitive preparations should be retained as much on the surface as possible, for experiment will show, the most striking difference between the same preparation spread on a paper of a firm texture and on an absorptive variety. The best kinds of paper, which are those known to the trade as hand-made and calendered papers, differ considerably on their two surfaces, one being much less absorbent than the other, which is the side that must be chosen as the one for spreading the sensitive washes over.

(91.) It was noticed by Mr. Talbot, in the very outset of his photographic experiments, that however carefully a paper might be prepared with the above materials,—and the same applies to all others,—it would sometimes turn out to be nearly, if not quite, insensible to Light in some parts of its surface. He thus describes this singular quality:—“Exposed to sunshine, this paper will exhibit large white spots of a very definite outline, where the preparing process has failed; the rest of the paper where it has succeeded turning black as rapidly as possible. Sometimes the spots are of a pale tint of cerulean blue, and are surrounded by exceedingly definite outlines of perfect whiteness, contrasting very much with the blackness of the part immediately succeeding.” There can be but one opinion as to the cause of this very annoying peculiarity. The chemical compound used, exists in two definite and different states in the light

and dark parts of the paper. We shall find, if we carefully examine the matter, that the same sheet of paper will absorb more moisture in some parts than it will do in others, consequently we shall have (to cite the present case) a larger quantity of salt in some places than in others: and when we apply the nitrate of silver, portions of the paper will become covered with the chloride of silver, having the required excess of the nitrate of silver, while others will consist of the pure chloride, or a double salt, the muriate of soda and silver. Sir John Herschel proposes to remedy this "by saturating the saline washes used, previous to their application, with chloride of silver. (Chloride of sodium will dissolve a considerable quantity of the chloride of silver.) By attending to this precaution, and by dividing the last wash of the nitrate into two of half the strength, applied one after the other, drying the paper between them, their occurrence may be almost entirely obviated." In my own experience I have found this method generally answer the desired object, but it appears to be somewhat injurious to the sensibility of the paper. If the saline wash is applied with a sponge, care being taken not to remove the pile of the paper, it will be found that we are less liable to these spots than when the paper is soaked in the solution.

(92.) A very pretty modification of these processes has been recommended by Sir John Herschel, which resulted from his experiments to ascertain how far organic matter was necessary to produce the change in the chloride and other salts of silver. A film of the chloride is precipitated on a glass plate, in the manner previously described, and carefully dried in the dark. This pure chloride of silver is scarcely sensible to the influence of ordinary daylight, unless by a very prolonged exposure; but if it is washed over with a solution of the nitrate of silver, it becomes exceedingly sensitive, and may be used for receiving pictures in the camera obscura. These are very interesting and well-defined negative pictures, which are direct or reversed according as looked at on the side which was exposed to

Light, or the opposite. By pouring over these pictures a solution of hyposulphite of soda, they disappear, but on washing them with pure water, and drying, they are restored, and assume much the air of a Daguerreotype, when laid on a black ground, and still more so when smoked at the back; so that its character is in fact changed from a negative to a positive picture. (*Herschel.*) It is necessary that the plate should be exposed wet, and when withdrawn plunged instantly into water.

(93.) The action of the solar radiations having produced the required impression, it becomes necessary to render these pictures permanent, that they should be subjected to some process, which should prevent the white parts from undergoing any change. The perfect fixing of the Photographic pictures depends upon the entire removal of the unchanged salt from the plate or paper employed: some solvent is therefore required. The best solvent for the chloride or iodide of silver is the hyposulphite of soda, for which we are indebted to Sir John Herschel. Some care is required in this fixing process, but with attention this salt will be found to be much more useful than any other agent. The drawing being produced, should be first soaked in clean water, to dissolve out as much as possible of the nitrate of silver. It is then to be immersed for a few minutes in water, to which a little common salt has been added, the object of which is to convert any portion of the nitrate that may remain in the paper into a chloride. When any nitrate of silver is present the hyposulphite changes it to a sulphuret, the brown colour of which is destructive to the beauty of the picture, and prevents its being used for multiplying originals. When nearly dry, it is to be brushed over, first on the face, and then on the back, with the solution of the hyposulphite of soda, and immediately immersed in clean water. Having been allowed to soak for a few minutes, it should be placed on a porcelain slab, and gently washed with a soft sponge

and clean water, until the fluid flows off without any sweetness of taste; the combination of the chloride of silver and the hyposulphite producing a salt,—hyposulphite of silver,—which is remarkable as producing a sensation of intense sweetness over the mouth. It is a peculiarity of this method of fixing, that nearly all the delicate parts which may appear to have suffered in the process, develop themselves again with considerable sharpness on drying.

(94.) A very curious process of fixing was first noticed by Sir John Herschel, and nearly about the same time dropped upon by myself, while endeavouring to fix some pictures produced by a positive process, to be described under the Iodides. It has the peculiarity of completely obliterating the picture, “reducing it to a state of perfectly *white paper*, on which the nicest examination (if the process be perfectly executed) can detect no trace, and in which it may be used for any other purpose, as drawing, writing, &c., being completely insensible to Light.” — (*Herschel*.) Where iodine is present, the paper becomes a deep yellow. This obliteration is effected by washing the picture with a solution of corrosive sublimate, soaking it in water, and drying it. Though invisible, the picture still exists, and may at any time be revived from its dormant state, by brushing it over with liquid hyposulphite of soda or caustic ammonia.

It should be noticed, that a very considerable difference will be found in the injury done to a photograph by the fixing process, according as it has been produced quickly under the action of a good sun, or by the prolonged influence of a more feeble light. Those produced in bright sunshine are not at all, or but slightly injured; whereas those which have been affected by a weak daylight, lose much of their sharpness, and indeed many parts are often destroyed.

(95.) We have now to consider the nature of the change produced on the salts of silver by solar influence,

about which it appears some misconception has existed. The following experiments will set the question in a clearer light. By examining the changes which take place on the oxide, nitrate and chloride of silver in connexion, we get a fairer representation of the chemical alterations than we should by any other arrangement.

(96.) OXIDE OF SILVER.—To a weak solution of nitrate of silver in distilled water a very dilute solution of pure baryta was added, and the resulting precipitated oxide of silver received upon plates of glass. When the whole of the oxide had fallen down, the fluid was removed very slowly, by means of a small glass siphon, so that the powder on the glass plates might not be disturbed. Without being removed from the vessel in which the precipitation was effected, the oxide was dried at a very moderate heat, and there resulted exceedingly thin films of the oxide of silver on the glass, quite free from all organic matter, every precaution being taken to prevent its presence.

(97.) These plates were exposed to full sunshine for periods varying from one to twenty-four hours, one half of them being covered with an opaque body. The brown oxide of silver (protoxide) was gradually darkened; so that after half an hour's exposure, the exposed part was a much deeper brown than that which had been covered. This darkening process was continued until a perfect black was produced, after which, by the prolonged action of sunshine, a very remarkable whitening of the oxide was observed to take place, and proceed slowly until it acquired a very fine olive colour.

(98.) On immersing one of these plates in strong ammonia, all the oxide which had been kept from the solar action was dissolved off, whereas the exposed part did not appear to be acted on. Another plate immersed in a solution of twenty grains of nitric acid in 300 grains of water, was acted on in precisely the same manner; the oxide being entirely removed from the unexposed portion

of the glass plate, whilst the changed part appeared to remain untouched. From this we might consequently infer that the oxide of silver had been reduced to the metallic state. Moderately strong nitric acid, dissolving the whole from the glass, seemed to render this in every way probable.

(99.) Metallic silver, in however fine a state of division it may be, conducts electricity; consequently it was expected that the changed oxide would conduct the current of a voltaic battery. One of the glass plates covered with oxide was made part of the circuit, between a single pair and a galvanometer of great delicacy; but not the slightest indication of any conducting power could be detected. This may have arisen from a want of perfect continuity.

(100.) Films of oxide of silver were darkened all over by long exposure to sunshine. One was placed in ammonia, and another in very dilute nitric acid. It was now discovered that the ammonia did dissolve a portion of the charged oxide; it became of a pale brown colour, and was found to hold silver in solution. The dilute nitric acid also dissolved off some oxide from the plate, as was shown by its becoming milky on the addition of muriatic acid. On adding some potash to the ammonia, and dissipating the ammonia by heat, a black precipitate was formed. The precipitate from nitric acid by potash was dark brown. The general characters of this oxide were the same as those of the suboxide of silver examined by M. Wöhler.

(101.) After having removed as much as possible from the glass plate, by solution of ammonia, there was still a film upon the surface of the glass, which upon drying became nearly black, appearing of a fine olive green colour when looked through. It was now ascertained that this film conducted the electric current, and on pouring over the plates nitric acid diluted with an equal quantity of water, the films were dissolved off with the formation of nitrous acid fumes.

(102.) These results prove that the influence of the

chemical rays (*actinism*) on the protoxide of silver, converts it first into a suboxide and into metallic silver. I have not been able, by the longest exposure to sunshine, to reduce all the suboxide to the state of metal, unless organic matter was present.

(103.) Pure protoxide of silver being spread whilst moist upon paper, by means of a camel-hair pencil, and carefully dried, passes, in the course of a few hours, if the sun shines strongly, into a perfect black, the whole of which dissolves off in ammonia. This salt precipitated by potash, the ammonia being dissipated by heat, gave upon reduction the exact formula of Wöhler's oxide (Ag. 2 O.).

(104.) By continuing the exposure of these papers for a few days, their colours were changed from black to olive. Ammonia dissolved nothing, and diluted nitric acid was equally inactive. In moderately strong nitric acid, however, the paper was almost immediately rendered white with the formation of nitrous acid fumes. Any analytical results from preparations on paper are so liable to error, from the inconstant character of the composition of the paper itself, that they are scarcely to be depended upon. But by very carefully drying two weighed pieces of paper until they lost no further weight, and even heating them up to a point but a little below that at which the paper would scorch, placing them both in warm tubes and hermetically sealing them, exposing one to the actinic influence, whilst the other was preserved in the dark, opening the tubes under the same circumstances, burning the papers at the same temperature, and weighing the ashes against each other, I succeeded in reducing the sources of error considerably; and the result was, in several experiments, that the actinized oxide lost in weight *very nearly* the weight of the oxygen of the oxide employed.

(105.) Several trials were made to ascertain if the films of oxide of silver on the glass plates lost weight upon darkening; but although some evidence was obtained that they did so, it must be admitted that it was not at all satisfactorily proved to be the case by this means. The



films seldom exceeded a grain in weight, and the pieces of glass upon which they were spread generally weighed 200 grains; it will therefore be easily conceived how difficult a thing it was, after an exposure of some hours to sunshine, and under all the varying conditions of temperature and atmospheric moisture, to decide with anything like accuracy the loss by weight of oxygen from the oxide employed; the more so as evidence was obtained to show that the finely divided metal had the property of condensing water within its pores with some rapidity. I cannot refrain from venturing to express my opinion, that the silver reduced by actinic power is different in many respects from silver brought to an equally fine state of division by mechanical means: it is an alotropic condition of silver.

(106.) The oxide of silver, as is well known, is soluble in ammonia; by exposing such a solution to the action of the atmosphere, a pellicle forms upon its surface, which Faraday considers a peculiar oxide. If this solution is spread over paper, and dried in the dark, I believe a similar oxide of silver is formed. This paper darkens by exposure to light with some rapidity, as does also the film formed on the surface of the ammonia. After darkening, it will be found that the darkened parts are no longer soluble in ammonia, or in diluted nitric acid, but that moderately strong nitric acid dissolves it with the formation of nitrous acid vapours. In this case, consequently, we may conclude that the oxide is reduced to the metallic state at once by the action of the sun's rays.

(107.) Perfectly pure silver, as is well known, does not combine with oxygen by exposure to the air; but silver reduced as above by solar action, becomes oxidised by exposure, and, after a short time, ammonia will dissolve off a considerable portion.

(108.) NITRATE OF SILVER.—Nitrate of silver does not change by the action of light, unless organic matter is present, for which it is so delicate a test, that Dr. John Davy recommended it as the most useful for ascertaining

the presence of minute quantities in a solution. It has been stated that the "nitric acid appears to be the agent which destroys the animal texture, and the black stain is owing to the separation of oxide of silver;"\* and this opinion has been very generally entertained. I am satisfied, however, that something more than this takes place, and that an actual combination of the organic body with the silver ensues.

(109.) Count Rumford appears to have been the first who noticed that carbon had the property of reducing the salts of gold and silver from their solutions, in *the dark*, at a temperature below that of boiling water; and that a similar precipitate of pure metal took place by exposure to the sun's rays. He inferred from this, that the "chemical properties attributed to Light" were due alone to the heating power of the sun's rays. The error of this has long been known, as experiments with the prismatic spectrum have shown that the rays in which the calorific power exists at its maximum have little effect in producing such reduction. The precipitation of the silver from the nitrate in solution takes place very speedily under the influence of the solar rays which have been deprived of their heat, by being passed through plates of alum or rock salt, and when the temperature of the solution is kept at 32° F.

(110.) Nitrate of silver dissolved in distilled water was spread on paper; it was allowed to darken to a chocolate-brown: ammonia now dissolved off the darkened surface, proving it to be in the condition of an oxide. The exposure being continued for some hours during very bright sunshine, a surface of a peculiar russet colour, and of a dirty appearance, results. Ammonia did not now possess the power of altering the colour; it removed some oxide from the paper, which arose from undecomposed nitrate of silver, protected by the superficial film from the action

\* Turner's Elements of Chemistry.

of the rays of the sun. But if the darkened paper was previously soaked in distilled water until all the free nitrate was dissolved out of it, neither ammonia nor dilute nitric acid separated any oxide, clearly showing that the darkened surface was metallic silver.

(111.) Some nitrate of silver in distilled water was boiled with a grain or two of animal gelatine for some hours in the dark; the solution became coloured a fine brown; but even after standing many hours no precipitation took place. Potash precipitated the oxide of a black-colour, which ammonia dissolved. The solution being of a brown colour, I am led to infer that this is a sub-oxide of silver.

(112.) A similar solution of nitrate of silver and gelatine was put into a stoppered bottle and exposed to sunshine; it speedily darkened, and in about two hours the solution was so opaque that the sun could scarcely be seen through it. Its colour was a greyish-green, which it retained during an exposure to very bright sunshine for five days. It was expected that an increase in the acid reaction of the solution might be detected during the progress of the precipitation. Such can scarcely be said to have been the case: the solution was repeatedly tested with litmus paper, without detecting any decided effect, even after the entire length of the exposure.

(113.) It was with difficulty that the precipitated matter could be separated from the solution; this was at length effected by subsidence, and it was found to be entirely soluble in ammonia, giving a reddish-brown solution. The bottle in which the solution had been placed was coated with a thin film, of an olive-coloured matter, transmitting green light, upon which neither ammonia nor very dilute nitric acid acted. By nitric acid diluted with an equal quantity of water, this film was very speedily dissolved, the bottle becoming filled with nitrous acid fumes. It is apparent from this experiment, that the first action of the solar rays is to liberate the protoxide of silver from its com-

bined acid, then to set free another proportional of oxygen, and that eventually the sub-oxide is entirely reduced to metallic silver.

(114.) CHLORIDE OF SILVER.—Perfectly pure chloride of silver was prepared by dissolving crystallised nitrate of silver in distilled water, which had been boiled with a little nitric acid, to ensure the absence of any organic matter; it was then precipitated by pure hydrochloric acid, well washed with distilled water, separated by subsidence and dried on glass in a sand bath. In diffused light this chloride changes colour very slowly, and eventually assumes only a light lead colour. In bright sunshine it darkens much more rapidly, and becomes brown by about one hour's exposure.

(115.) Under the influence of the prismatic spectrum, two very decided colours are produced on the pure chloride of silver, a blue or fine rich lead colour, by the space between the most refrangible green and the extreme edge of the violet rays, beyond which, for some distance, the same colour occurs, but gradually lowered until it becomes a mere tint of a lilac hue, at a distance beyond the visible spectrum, equal to one-third its length, and over the space occupied by the least refrangible rays, a brown impression passing into a decided red under the red rays is slowly produced.

(116.) It has been shown by numerous photographers, that a slight excess of the nitrate of silver was necessary to exalt the power of the chloride to change, by the action of chemical radiations. It was important to ascertain the cause of this. Three pieces of glass covered with films of chloride of silver, by subsidence, were selected; one was exposed quite dry, another moistened with distilled water, and the third with a solution of nitrate of silver. The action was most rapid on that glass wetted with the silver solution; the next in order was the moistened one. In an hour they were all, however, darkened to, as nearly as possible, the same shade of colour.

(117.) The glass plate over which the wash of nitrate of silver had been applied, was washed in distilled water to remove any of that salt that might remain undecomposed. The three pieces of glass, with their darkened films, were then boiled separately in nitric acid, diluted with double its quantity of water. The colours of the plates were but slightly changed. The liquids were then examined for silver, and in that alone in which the plate on which the nitrate had been spread was any detected. It was evident that the nitric acid had either dissolved off oxide of silver, or it had oxidised metallic silver and then dissolved it. The films on the other plates were not changed in colour by the application of either ammonia or hyposulphite of soda.

(118.) Three similar plates of glass covered with films of chloride of silver were placed in jars of pure hydrogen and nitrogen gases, and in atmospheric air, and then exposed to bright diffused Light. The object of this was to ascertain if the nitrogen of the acid, or hydrogen of the water, were likely to assist the change in any way. The chloride in the nitrogen and the atmospheric air darkened equally in equal times. The first action of the hydrogen on the chloride of silver was to reduce it to the state of metal over the surface. But as soon as the chloride began to darken, this bright metallic film and the whole darkened equally, but to a deeper tint than either of the others. These plates, as in the former case, were boiled in diluted acid, from which experiment I ascertained that the hydrogen plate alone gave any evidence of the presence of oxide of silver or revived metal.

(119.) It may appear that this metal was produced by the hydrogen independently of the *actinic* or chemical radiation; but I find when chloride of silver is plunged into hydrogen gas in bright sunshine, that no reduction of the chloride due directly to the hydrogen takes place: yet most distinct evidence of the presence of metallic silver after darkening has been obtained. We thus learn that

the advantage of the nitrate of silver over the chloride is, that it is more readily reduced to the metallic state than the chloride; and that the accelerating power of moisture is due to the decomposition of water, and the influence of nascent hydrogen in reducing the argentine salt.

(120.) The principal point now to ascertain was the condition of the chloride of silver after it had been thoroughly darkened by exposure. Many experiments were tried in various ways, but to the most satisfactory only I will confine attention. Pure chloride of silver was prepared with great care, well washed with boiling distilled water, until neither nitrate of silver nor muriatic acid produced any precipitate, and then dried. Five grains of the salt were put into a long test tube full of distilled water, and placed in the sunshine to darken, the powder being frequently moved that every part might be acted upon by the sun's rays. It was found, even after an exposure of a few minutes, that the water contained chloride; it became opaque on the addition of nitrate of silver, and this very gradually increased as the chloride darkened. The darkening process was continued for several hours, after which the solution was filtered to free it from chloride of silver, and nitrate of silver added to the filtered solution; this precipitated chloride of silver, which, when collected, dried, and weighed, gave 1.4 grains on one occasion, 1 grain on another, and 1.5 grains on a third trial. From this it is evident that chlorine is liberated during the process of darkening.

(121.) The exposure in the water was in another case continued for several days, but no greater degree of darkening occurred; but a curious fact was noticed. It was found that during the night nearly all the chlorine which had been liberated during the day was recombined, and that the darkened powder became lighter. This is an analogous case to placing pure chloride of silver in a tube filled with chlorine, which was first pointed out by Mr. Shaw. The chloride will darken by exposure in sunshine;

the chlorine again attacks the silver in the dark; and restores it to its white colour.

(122.) In these experiments the presence of organic matter had been carefully avoided. It now became necessary to inquire into the condition of the chloride of silver darkening by the solar rays on paper. Bath post-paper, highly glazed, was covered with chloride of silver in the usual way, all free nitrate of silver being washed off. The paper was then exposed to sunshine for forty-eight hours, in which time it had passed to a fine olive-brown metallic colour. The paper was now cut into pieces; some parts were immersed in very dilute nitric acid, which produced no change; others in ammonia, which had not the slightest effect upon them; therefore it was evident that no oxide of silver was present. On putting fragments of the paper into nitric acid diluted with equal parts of water, all the darkened portion was rapidly dissolved off, and the paper was left of a lilac colour. Hence we have very satisfactory proof that metallic silver is eventually formed on the surface of the chloridated photographic papers, and that the under sensitive surface is preserved in the condition of a subchloride of silver by the opacity of the superficial coat.

(123.) From other experiments, I am inclined to believe that the first action of the solar ray is to liberate one half the combined chlorine, which is very readily, moisture being present, replaced by oxygen. By the continued action of the exciting cause the oxide is decomposed, and metallic silver in a state of fine division is formed over the surface.

(124.) It must not be forgotten that whenever organic matter is present, even the stable oxide of silver, chloride and iodide readily give way under the chemical action of the solar rays, and metallic silver is very readily formed.

(125.) The absorption of oxygen, or rather its combination with the decomposing chloride, is proved by another very easy experiment. Some pure chloride of

silver was arranged in a bent tube closed at one end, and the other end immersed in a bottle of distilled water. In this state the chloride was exposed for many days to the action of sunshine, during which time it was frequently shaken, for the purpose of exposing the whole of the powder to its influence. As the chloride darkened the water rose into the tube, and it gave a precipitate of chloride of silver on the addition of the nitrate, thus appearing to prove the substitution of oxygen for chlorine under the agency of solar radiation. It was quite evident that some absorption of atmospheric air had taken place. This explanation will also serve for the iodide, bromide, and some other salts of this metal.

(126.) IODIDE OF SILVER. — The preceding experiments on the chloride of silver, as I have said, apply equally to the iodide, the action in all cases being similar, so that if we substitute iodine or bromine for chlorine, the rationale is correctly represented. Perfectly pure iodide of silver may be exposed for a long period to Light without undergoing any visible change; except, perhaps, in some cases a more decided yellow colour than is usual to it comes on; but this appears to depend on the influence of the calorific rays, as the same effect is produced by exposing it to a very moderate degree of heat. If, however, a slight excess of the nitrate of silver in solution is present, the iodide becomes infinitely more sensitive than the chloride of silver.

(127.) *Prismatic Analysis.* — The spectrum impressed upon a paper prepared with a weak solution of the iodide of potassium presents some very remarkable peculiarities. The maximum of intensity is found at the edge of the most refrangible violet rays, or a little beyond it: Sir John Herschel places it at a short distance beyond. The chemical action rarely extends below the green ray; hence the iodide of silver imperfectly receives impressions from foliage, or any bodies radiating yellow light. I have found that it varies slightly according to the kind of paper used,



and also with the quantity of free nitrate of silver present. The action commences at a point nearly coincident with the mean red of the luminous spectrum, where it gives a dull ash or lead colour, while the most refrangible rays impress a ruddy snuff-brown, the change of tint coming on rather suddenly about the end of the blue or the beginning of the violet rays of the luminous spectrum. (*Herschel.*) Beyond the extreme violet ray, or rather beyond the maximum point, the action rapidly diminishes; but the darkening produced by these invisible rays extends over a small space beyond the point at which they cease to act on the chloride of silver.

(128.) *Photographic Application.* — The use of papers prepared with the iodide of silver alone can only be recommended as affording a very pleasing variety of pictures, having a primrose instead of a white ground. The best proportions in which the respective salts of iodine and of silver can be used, according to my own experience, are the following: — Twenty grains of nitrate of silver should be dissolved in half an ounce of distilled water, and this, with a very soft brush, carefully applied over the paper, and allowed to dry. Ten grains of the iodide of potassium dissolved in the same quantity of water, is next to be applied, and the paper quickly dried near the fire, care being taken, not to warm it too much, as heat changes this salt from its delicate primrose colour to a pink or rosy brown, which, although still sensitive, is not so much so as the parts which are not so altered.

(129.) In combination with other reagents, the iodide of silver becomes exquisitely sensitive, and from two such combinations, gallic acid and the ferrocyanide of potassium, result two exceedingly sensitive photographic applications. To these we must now direct attention; taking, in the first place, Mr. Talbot's description of the process, which he has named the Calotype.

(130.) *THE CALOTYPE PROCESS.* — *Preparation of the*

*Paper.* Take a sheet of the best writing-paper, having a smooth surface, and a close and even texture. The watermark, if any, should be cut off lest it should injure the appearance of the picture. Dissolve 100 grains of crystallized nitrate of silver in six ounces of distilled water. Wash the paper with this solution with a soft brush on one side, and put a mark on that side whereby to know it again. Dry the paper cautiously at a distant fire, or else let it dry spontaneously in a dark room. When dry, or nearly so, dip it into a solution of iodide of potassium, containing 500 grains of that salt dissolved in one pint of water, and let it stay two or three minutes in the solution. Then dip it into a vessel of water, dry it lightly with blotting-paper, and finish drying it at a fire, which will not injure it even if held pretty near; or else it may be left to dry spontaneously. All this is best done in the evening by candlelight. The paper so far prepared Mr. Talbot calls *iodized paper*, because it has a uniform pale yellow coating of iodide of silver. It is scarcely sensitive to Light, but nevertheless it ought to be kept in a portfolio or a drawer until wanted for use. It may be kept for any length of time without spoiling or undergoing any change if protected from the Light. When the paper is required for use, take a sheet of it, and wash it with a liquid prepared in the following manner:—

Dissolve 100 grains of crystallized nitrate of silver in two ounces of distilled water; add to this solution one-sixth of its volume of strong acetic acid. Let this mixture be called A.

Make a saturated solution of crystallised gallic acid in cold distilled water. The quantity dissolved is very small. Call this solution B.

Mix together the liquids A and B in equal volumes, but only mix a small quantity of them at a time, because the mixture does not keep long without spoiling. Mr. Talbot calls this mixture the gallo-nitrate of silver. This solution must be washed over the iodized paper on the side

marked, and, being allowed to remain upon it for half a minute, it must be dipped into water, and then dried lightly with blotting paper. This operation in particular requires the exclusion of daylight; and although the paper thus prepared has been found to keep for a short time, it is advisable to use it within a few hours, as it is sometimes rendered useless by spontaneous change in the dark.

Paper thus prepared is exquisitely sensitive to Light, exposure of less than a second to diffused daylight being quite sufficient to set up the process of change. If a piece of this paper is partly covered, and the other part exposed to daylight for the briefest possible period of time, a very decided impression will be made. This impression is latent and invisible. If, however, the paper be placed aside in the dark, it will gradually develope itself; or it may be brought out immediately by being again washed over with the gallo-nitrate of silver, and held at a short distance from the fire, by which the exposed portions become brown, the covered parts remaining of their original colour.

The pictures being thus procured, are to be fixed by washing in clean water, and lightly drying between blotting paper, after which they are to be soaked in a solution of the hyposulphite of soda for a few minutes; after this they are to be again dipped into water, allowed to remain until all the soluble salt is removed, and then finally dried.

(131.) The discovery of the extraordinary property of the gallic acid, in increasing the sensibility of the iodide of silver, is amongst the numerous claims which Mr. Talbot has made to discoveries in the photographic art. It must however be remembered that Sir J. Herschel used gallic acid, but not successfully, and that previously the infusion of galls had been employed by the Rev. Mr. Read with success. The calotype process, as described and practised by Mr. Fox Talbot, yields pictures of exquisite beauty, which preserve, with the utmost fidelity, not only

the bold outline of the object, but its minute and delicate details. The charm of colour alone is wanting, and this is compensated by the harmony of the whole. The gradation of shadow is often given in a really wonderful manner, the lights of the picture decaying in soft and almost invisible tints into the deepest shades; the middle lights being preserved in a manner, which renders these pictures the most truthful studies for the artist who desires to fix the charms of Nature on his canvass, rather than those, so called, artistic effects, which are the bane of modern art and destructive alike to truth and good taste.\*

\* Mr. Fox Talbot has, in his patent, claimed the use of gallic acid as being his own discovery, and he has enforced his claim by legal proceedings in several cases. Now, Mr. Talbot's patent was sealed on the 8th February, 1841. On the 10th of April, 1839,—that is, nearly two years previously to the date of this patent,—Mr. E. W. Brayley exhibited and explained at one of the soirées of the London Institution pictures obtained by the Rev. J. B. Reade, F.R.S., prepared by the following process, as described by Mr. Reade on the 9th March, 1839, in a letter to Mr. Brayley.

“The more important process, and one probably different from any hitherto employed, consists in washing good writing paper with a strong solution of nitrate of silver, containing not less than 8 grains to every drachm of distilled water. The paper thus prepared is placed in the dark, and allowed to dry gradually. When perfectly dry, and *just before it is used, I wash it with an infusion of galls*, prepared according to the Pharmacopeia, and immediately, even while it is yet wet, throw upon it the image of microscopic objects by means of the solar microscope.

“It will be unnecessary for me to describe the effect, as I am able to illustrate it by drawings thus produced. I will only add, with respect to the time, that the drawing of the flea was perfected in less than five minutes, and the section of cane, and the spiral vessels of the stalk of common rhubarb, in about eight or ten minutes. *These drawings are fixed by hyposulphite of soda*. They may also be fixed by immersing them for a few minutes in weak salt and water, and then, for the same time, in a weak solution of hydriodate of potash. The drawing of the *Trientalis Europea* was fixed by the latter method: it was procured in half a minute, and the difference in the colour of the ground is due to this rapid and powerful action of the solar rays. This paper may be successfully used in the camera obscura.

“Farther experiments must determine the nature of this very sensitive argentine preparation. I presume that it is a gallate or tannate of

(132.) The calotype picture is a *negative one*,—that is, the shadows are represented by lights, and lights by shadows; also reverse, as it regards right and left; but when fixed by the above process, a great number of *positive* copies, correct in all respects, may be taken from it. To do this, it is only necessary that the drawing be placed with its face against the sensitive side of a piece of ordinary photographic paper, and being pressed into close contact by a board below, and a glass above, exposed for a short time to good sunshine. This period, of course, varies with the transparency of the original calotype, and the brilliancy of the sunshine. It must be remembered that the Light has to permeate a piece of paper, the yellow tint of which offers considerable interruption to the free passage of those rays which are active in producing chemical change; we must therefore be exceedingly careful to preserve the prepared sheet of as pale and uniform a tint as possible. All processes on paper, which require the production of the positive from the negative drawing, are, in one particular, alike defective. The irregularities of the paper itself are copied with the picture. This is only to be remedied by substituting some more transparent material, or getting a paper manufactured superior to any which is at present in the market, uniting transparency with firmness of texture and evenness of surface.

(133.) With a view to overcome these objections, the “WAX-PAPER PROCESS” has been introduced. This consists in saturating fine writing-paper with white wax, by placing the sheet on a hot plate, and rubbing it with wax. This waxed paper is placed in a solution of iodide of potassium, and in a short time the salt enters into combination with the wax. When this union is complete, the paper is readily covered with the iodide of silver, by

silver, and, if so, it will be interesting to you to know that what has hitherto been looked upon as a common chemical compound is produced or suspended at pleasure by our command over the rays of light.”

floating it upon a bath of nitrate of silver. It is then excited in the ordinary way with the combined gallic acid and nitrate of silver. (There are many manipulatory details which do not properly belong to this volume, which will be found fully described in my Treatise on Photography.)

(134.) Glass plates covered with albumen, in which some iodide of potassium has been dissolved, have been most successfully employed for obtaining the negative picture. The glass having been carefully coated with the strained white of egg and iodine salt, is dried by a gentle heat: it is then immersed in a solution of nitrate of silver, and thus coated with iodide of silver. When excited by the gallic acid, this preparation receives beautiful images in the camera obscura, and the positive copies, obtained from these negatives, are free of the defects of those obtained from the paper. The COLLODION PROCESS naturally forms a section of this division; but as some of the peculiarities require very exact attention, it is deferred to a future page for separate consideration.

(135.) The part which the gallic acid plays in these processes is sufficiently obvious. The chemical action of this acid on most of the metallic salts is well known. It seizes readily upon the oxygen of the metallic oxides, and precipitates the metal in a pure state from its combination with even the powerful acids. Since the attention of chemists has been more forcibly directed to the several phenomena connected with alterations produced in chemical compounds by luminous agency, numerous very curious instances have been discovered of the continuation in the dark of that change which Light has begun to produce. If we unite a solution of gallic acid and nitrate of silver, even in weak diffused Light, it will be found that a precipitate is almost immediately formed, whereas the same solution will often remain clear for many hours in the dark. If we apply this mixture whilst clear to any preparation of silver on paper, which is sufficiently sensitive, or has

been exposed to Light for a sufficient time for a change to have commenced, the formation of metallic silver in a state of fine division, is carried on over those parts on which the solar rays have exerted their influence, with an energy equal to the intensity of the radiations which have acted on the several parts, or, in other words, to the degree of change which the preparation has undergone; while, for some time, the parts in shadow, exerting no extraordinary power, remain clear and unchanged. To preserve these parts quite transparent, it is therefore advantageous to accelerate the decomposition over the other parts by the aid of warmth; and hence it is advised that the drawing be held, for a few seconds, at a short distance from the fire. The gradual development of the calotype photographic picture, in any of its varieties, is, to a person who witnesses it for the first time, a phenomenon of a remarkable, indeed almost magical, character. Some experience is required to check the action of the gallo-nitrate of silver at the proper time: if it has not remained on the paper long enough, the opacity of the dark parts is not sufficient to insure good positive copies; and if it remains too long, the light portions begin to darken, and, as this darkening proceeds with rapidity, the picture is soon rendered useless as an original from which copies can be taken.

(136.) The calotype process may, for many purposes, be most advantageously simplified; but before we proceed to this, it will be interesting to know the particular action of pure gallic acid upon several varieties of argenterous preparations which have been acted on by Light. Paper simply washed over with the *nitrate of silver*, and exposed for two minutes in the camera obscura, which was the time allowed in all cases, unless it is stated to be otherwise, gave, when washed over in the dark, a very faint image. The *chloride of silver* on paper gave, under the same treatment, a good picture; but it wanted clearness and depth of colour. The *oxide* and also the *bromide*

*of silver* on paper gave, by an exposure of only one minute, a very beautiful picture. *Tartrate of silver*, even when the paper upon which it was spread was exposed for eight minutes, appeared insensible to the exciting power of the gallic acid. *Oxalate of silver*, exposed in the camera for ten minutes, gave an exceedingly faint representation. *Phosphate of silver* yielded a well marked picture. *Carbonate of silver* in five minutes afforded a tolerable good result. Several of the compounds of benzoine, as *formo-benzoate of silver*, the *benzoate of silver*, and others, gave exceedingly pleasing pictures; and one, in particular, the *formo-benzoate of ammonia*, and the nitrate of silver, a photograph quite equal to those produced by Mr. Talbot's process; and I recommend it for all purposes in which extreme sensibility, as for portraiture, is not required. Neither the pure *cyanide of silver*, nor the *ferrocyanide*, gave any sign of change after an exposure of five minutes, whether washed with pure gallic acid or with the gallo-nitrate of silver.\* A great many other preparations of silver have been tried, and, as far as my researches have gone, it appears that whenever the salt used is sufficiently under the influence of sunshine to undergo a change, however slight it may be, the gallic acid will carry on the action in the dark and without heat. Gallic acid is therefore a most delicate test for any change produced by luminous radiation.

(137.) Mr. Channing of Boston, and Mr. C. Cundell of London†, appear to have been the first to publish methods by which the calotype process could be simplified. The most satisfactory preparations which I have yet employed are the *bromide of silver*, formed by washing paper first

\* Mr. Channing of Boston, in a paper on Photographic Manipulation, in the American Journal of Arts and Sciences, July 1842, gives the following series as being capable of being brought out by gallic acid:—  
“Iodide with chloride, iodide, iodide with bromide, bromide, bromide with chloride, fluoride, nitrate, ferrocyanide, sulphocyanide, cyanide.”

† Philosophical Magazine, May, 1844.



with a solution of silver, as above, and then with a solution of twenty grains of the bromide of potassium in one ounce of water; and, as I have before stated, the *formo-benzoate of ammonia* and silver, formed by washing the paper first with the formo-benzoate, in the proportion of fifteen grains of the salt to one ounce of water, and then with the nitrate of silver, as above. In good sunshine an edifice may be beautifully copied by either of the two last processes in a minute, and by the others in about two minutes. To preserve these pictures of a clear white, it is advisable that they should be soaked in water for a minute, previously to the application of the gallic acid.

(138.) The calotype paper is capable of being used for the production of positive photographs by one process. Mr. Talbot, in his specification, thus describes his method:—"A sheet of sensitive calotype paper is exposed to the daylight for a few seconds, or until a visible discoloration or browning of its surface takes place; then it is to be dipped into a solution of iodide of potassium, consisting of 500 grains to one pint of water. The visible discoloration is apparently removed by this immersion; such, however, is not really the case, for if the paper were dipped into a solution of gallo-nitrate of silver, it would speedily blacken all over. When the paper is removed from the iodide of potassium, it is washed in water, and dried with blotting paper. It is then placed in the camera obscura, and, after five or ten minutes, it is removed therefrom, and washed with gallo-nitrate of silver, and warmed, as before directed. Engravings may be copied in the same way, and positive copies of them produced, but reversed from right to left. For this purpose a sheet of calotype paper is exposed to the daylight to darken it, as before mentioned; but it should be darkened rather more than when intended to be acted upon in the camera. The engraving and the calotype paper must be pressed into contact by screws or otherwise, and placed in the sunshine, and the copy will be produced in a few minutes. If the copy is not suffi-

ently distinct, it must be strengthened by means of gallo-nitrate of silver.\*

(139.) No other process upon paper, which has yet been discovered, is sufficiently sensitive to luminous agency to admit of its being used for taking portraits from the life. Portraits of considerable fidelity may be procured, by paying strict attention to the improved directions for preparing the calotype paper. For this purpose, a camera, the focal length of whose lens is not more than three or four times the size of the aperture, should be used; and the head of the person whose portrait is to be taken must be kept as steady as possible; and, upon pointing the camera at it, an image is received on the sensitive calotype paper. No very satisfactory result can be expected unless the paper is sufficiently sensitive to give a good image in twenty or thirty seconds.

(140.) IODIDE OF SILVER AND FERROCYANIDE OF POTASSIUM.—At the meeting of the British Association in 1841, at Plymouth, I communicated to the Chemical Section a method which I had discovered of preparing a highly-sensitive paper, with the iodide of silver and the ferrocyanate of potash. It will be found that paper prepared with the iodide of silver, and then washed with a solution of the ferrocyanide of potassium, will blacken instantly on being exposed to the sun's rays. This effect will take place with the greatest rapidity, when the iodide of silver on the paper is as free from admixture as possible. Perfectly pure iodide of silver, as already remarked, does not appear to undergo any change by exposure. Under the prismatic spectrum, the space covered by the red rays is rendered very yellow, an effect due to the heat of those rays alone. Gallic acid gives evidence of some disturbance beyond this having taken place, over that part on which the more refrangible rays fell, by producing in the dark various shades of darkness. If, however, upon some pure iodide

\* Repertory of Patent Inventions.

of silver, spread out on glass, and exposed to sunshine, we drop a little of a solution of the ferrocyanide of potassium, an instantaneous darkness will take place and extend, in different degrees, over the whole space moistened by that salt.

(141.) The most successful form of manipulation is the following:—A piece of well-glazed letter-paper is washed over on one side with a solution of nitrate of silver — two drachms to one ounce of distilled water. It is then dried at a little distance from a warm fire, as speedily as possible. It is next washed over with a solution of the iodide of potassium — one drachm to one ounce of water — and being placed upon a smooth board, or a porcelain slab, pure water is poured slowly and uniformly over the paper to wash away any soluble salts. It may be used immediately, or dried, and kept for future use. To use this paper, it is washed over with a saturated solution of the ferrocyanide of potassium (*yellow prussiate*), lightly dried with blotting paper, and placed in the camera. A few minutes are quite sufficient to give a very beautiful negative picture in the camera obscura. Leaves of plants or engravings are copied with very great sharpness of outline, by the exposure of a single moment to sunshine.

I stated in my first announcement of this process, that if the paper when washed with the solution of the ferrocyanide was dried it was insensible to solar agency. If, by high drying, all the hygrometric moisture is removed from the paper, this is pretty nearly true; but, under the ordinary conditions, the paper will change with tolerable rapidity, but not so rapidly as when wet, nor does it eventually arrive at such a degree of blackness.

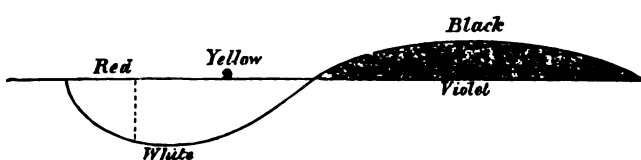
(142.) Extremely rapid as the change which takes place is, it may be very much quickened by first bringing on a degree of oxidation on the iodide of silver, either by Heat or Light. If the paper is allowed to brown under the influence of either of these elements, and then washed with the solution of the ferrocyanide, the change is almost

instantaneous. It is, however, unfortunate that this previous darkening interferes with the transparency of the paper so much, that positive copies cannot be obtained from these negative photographs.

(143.) The fixing of these photographs appears to be a matter of some uncertainty. It frequently happens that different specimens, all fixed by the same process, have different degrees of permanence, some of them fading very rapidly, and others enduring for a long time, without the slightest appearance of change. This arises from the obstinate retention of a portion of the ferrocyanide in the paper, the presence of the smallest quantity being eventually fatal to the picture. This action of the ferrocyanide of potassium was first pointed out by Sir John Herschel, who used this salt as a fixing agent; but he soon abandoned it on this account. The most successful mode is to soak the photograph for some time in warm water, which should be frequently changed, after which it should be brushed over on both sides with a weak solution of the iodide of potassium, and then again soaked in cold water for five or ten minutes, and dried.

(144.) *Prismatic Analysis.*—The spectrum produced upon the iodide of silver has been already described (127). After the application of the ferrocyanide of potassium, the paper blackens with extreme rapidity, the darkening process commencing in the violet rays, and extending over the whole space, occupied by the invisible chemical rays, and all the visible spectrum down to the extreme red rays. If removed as soon as the first darkening is seen to take place, a coloured spectrum will be found impressed, the red rays impressing a red colour, and the blue ones blue. In a short time a bleaching action comes on under the red rays, and extends upwards to the green. In the first action there is no evidence of any protecting influence in the extreme red ray; but when the bleaching effect is set up, the space occupied by the extreme red ray is maintained perfectly dark. I have been very kindly favoured

with a prismatic analysis from Sir John Herschel, which quite confirms my own results,—the spectrum this distinguished philosopher obtained may be represented by the following curve — the maximum and minimum, or rather the positive and negative, effect being shown.



(145.) Advantage has been taken of this bleaching property for the production of positive photographs by the first process. The plan pursued is, essentially, to darken the paper after the application of the ferrocyanate, and then to throw the balance in favour of the whitening effect, by washing over the paper with a tolerably strong solution of the iodide of potassium. Some processes, which are much more certain, and which give more permanent pictures, will presently be described.

(146.) The increased sensibility of this paper appears to depend on the united decomposition of the ferrocyanide of potassium and the iodide of silver. It is well known that the ferrocyanide of potassium is decomposed by prolonged exposure to the sun's rays, and a portion of prussian blue formed. It will be found that this decomposition is brought about with much greater rapidity, if iodide of potassium is mixed with the ferrocyanide; and this appears to be the case with most of the metallic iodides: with the iodide of silver this is very decided. Chemical philosophy affords us numerous examples, of the power which one body possesses of setting up an action similar to its own, in bodies brought into contact with it. Here we have two bodies in, what appears to be, almost chemical union, each one subject to change under solar power, exerting this *catalytic* influence, as it has been called, upon each other.

(147.) The ferrocyanide of potassium will, in all probability, be found equally useful in quickening the change upon other photographic materials. I find that it accelerates the darkening action on the bromide of silver considerably; and it acts powerfully upon the chloride under some conditions.

(148.) Positive Photographs formed by the Salts of Iodine. — If photographic paper, which has been darkened by exposure, is washed over with the iodide of potassium, it is speedily whitened by the solar rays upon subsequent exposure. The interesting character of the photographic processes founded upon this peculiarity led me to pay considerable attention to them. The results of my inquiries were published at the time in the "Philosophical Magazine,"\* since which nothing has been added to our knowledge of the subject.

(149.) To avoid unnecessarily complicating this part of my treatise, I shall refrain from entering into that very minute detail which is given in the paper above referred to, and confine myself to an explanation of the best mode of preparing a good photographic paper, on which perfect pictures may be produced in the camera or otherwise, having their lights and shadows correct as in nature by one operation. It is necessary to remark, that more exact attention is required in the preparation of this kind of paper than in almost any other; very trifling differences in the proportions of the ingredients used, and in the time occupied in the first darkening process, completely changing the result, as will be hereafter explained.

(150.) In preparing this kind of paper, almost any of the sensitive salts of silver may be used. Dr. Fyfe prefers the phosphate of silver. Lassaigne, Bayard, and Talbot use the chloride of silver. Verignon, however, recommends a combination of the chloride and bromide of silver.

\* Philosophical Magazine, Vol. xvii. No. 109., September, 1840.

My own experience is much in favour of the chloride. Hydro-chloride of ammonia and chloride of barium produce much better effects than any other salts in the production of the chloride of silver, the bleaching action being more easily excited, and the resulting pictures being of a more beautiful character.

Good letter paper is soaked for five or ten minutes in solutions of either of the above salts — forty grains of the salt to four ounces of water. Each sheet is then carefully removed, and being laid on a porcelain or marble slab, gently wiped over with very clean linen, and then dried. When dry, the paper being pinned out upon a board, it is washed over with the following solution : —

Take of crystallised nitrate of silver 120 grains, and dissolve it in twelve fluid drachms of distilled water; to this solution add four fluid drachms of alcohol, which will render the mixture opaque. After a few hours, a minute quantity of a dark precipitate falls, which must be separated by the filter.

This solution must be applied with a very soft sponge brush, boldly, but lightly, over one surface, and the paper carried directly into the sunshine. It is instantly changed, but usually it darkens at first very unequally, owing to the irregular absorption of the fluid by the paper. After it has been exposed for a few minutes, it is removed, and being again washed over with the argentine solution, it is a second time exposed, and kept in the sunshine, until a very fine chocolate brown colour is uniformly produced. It is then dried in the dark and preserved for use: it seldom happens that the paper is exposed sufficiently long to dry it perfectly.

(151.) It is necessary that great attention should be paid to the character of the Light to which, in this part of the process, these papers are submitted. The morning sun should be chosen, and a perfectly cloudless sky, if possible. It may appear unlikely, but nothing is really more true,

than, that these papers indicate to the practised eye, during the bleaching operation, the effects of every cloud which has obscured the sun's disc during the darkening process. A peculiar film, as if the washes had been applied with a dirty brush, is produced by every such check.

(152.) To use the papers thus prepared, it is required that they should be washed over with some iodide, and exposed to the sun's influence wet. The iodide of potassium, being the salt which is most easily obtained, will be generally preferred. It is very difficult to decide on the best proportions in which this salt should be used, the difference of a few grains only, wonderfully altering the result; in general, about 30 grains of a pure salt to one ounce of water, will be found to produce the best effect. In some experiments instituted to settle this important point, it was found that papers washed with a solution containing 100 grains to the ounce, required twelve minutes to bleach in the direct rays of the sun; whereas, papers washed in a solution of the strength above recommended, took but four minutes. For the camera obscura I would recommend the use of the iodide of barium, beyond every other preparation; and if by throwing down some of the baryta by a drop or two of dilute sulphuric acid, we set free a little hydriodic acid, it acts much more energetically on the darkened paper; giving in the camera, provided a good clear image is formed, a very beautiful positive picture in less than half an hour. When engravings are required to be copied, which they may be most beautifully by this process, they should be soaked in water, and superimposed on the photographic paper quite wet. The object of this is two-fold—to insure transparency, and the closest possible contact, the interposition of even films of air interfering with the result. Although it may appear, that there is much which is perplexing in this process, a little attention will soon render any one perfect in the manipulatory details, and then the results are certain. Pictures taken from nature with the camera in this manner, possess ex-



treme beauty. The fine contrast of the shadows with the lights, give them the character of finished *sæpia* drawings; and the gradations of tint, corresponding with the amount of Light radiated from different objects, are very pleasing.

(153.) These drawings may be most perfectly fixed, provided they are kept in a portfolio, and only exposed to the sunshine *occasionally*, by washing them in clean water only, which removes all the iodide that has not been decomposed. If, however, the drawings so fixed are exposed continually to Light and to the influence of atmospheric changes, they slowly fade out, and in a month or two no trace of a picture remains. This may be thus explained:— If a darkened paper is washed over with an iodide and exposed to sunshine, it is at first bleached, becoming yellow; then, if long exposed, it again darkens. If in this state it is put aside in the dark, it will in a few days be completely bleached; by exposure to sunshine it may be again darkened, but not so readily as at first, and the yellow colour is again restored in the dark.

(154.) If a darkened paper, bleached by an iodide and sunshine, again darkened, and then placed in a bottle of water, the yellow colour is much more quickly restored, and bubbles of gas will escape freely, which will be found on examination to be oxygen. If placed in an exhausted vessel and hermetically sealed, the drawings thus formed are quite permanent, however much they may be exposed to sunshine. From this it is evident that the gradual fading arises from the influence of atmospheric moisture. The water is slowly decomposed under luminous influence, the hydrogen unites with the iodine to form hydriodic acid, which converts the darkened portion (which is finely divided silver) again into the yellow iodide of silver.

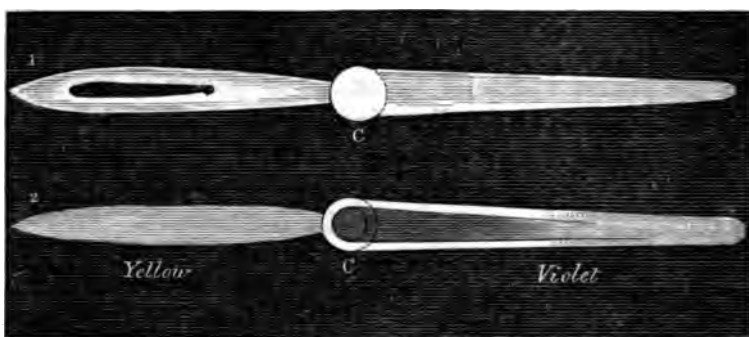
(155.) A few interesting experiments will place this question in a much clearer light. Precipitate with any iodine salt, iodide of silver from a solution of the nitrate, and expose the vessel containing it, liquid and all, to sun-

shine. The exposed surfaces of the iodide will blacken; remove the vessel into the dark, and after a few hours all the blackness will disappear: we may thus continually restore and remove the blackness at pleasure. The next experiment not only illustrates the phenomenon we are considering, but it further shows in a very marked manner, the influence of sunshine in producing chemical change. In one watch-glass was placed a solution of the nitrate of silver; in another, a solution of the iodide of potassium. The two glasses were connected by a filament of cotton, and a circuit made up with a piece of platina wire. This little arrangement was exposed to Light; and in a very short time iodine was liberated in one glass, and the yellow iodide of silver formed in the other, which blackened as quickly as it formed. A similar arrangement was placed in the dark. Iodine was slowly liberated; *no iodide of silver formed*, but around the wire, in the glass containing the silver solution, was a beautiful crystallisation of metallic silver. If the watch-glasses in which the processes of decomposition have taken place, be placed in the dark, it will be found in a few hours, that the solution which has become brown from the liberation of iodine, again gets gradually clear, and the darkened precipitate is converted into the yellow iodide of silver. The power of the sun's rays in influencing or disposing chemical affinity, is very marked in these experiments.

(156.) *Prismatic Analysis*.—The bleaching action on these papers is carried on by the influence of the blue and the more refrangible rays; but at the same time the least refrangible portion of the spectrum acts powerfully on the prepared surface, and induces an *extreme degree of blackness*. This peculiar and complex action has been much more fully examined by Sir John Herschel, who repeated the analysis with papers prepared by myself.\* When a

\* Sir John Herschel on the Action of the Rays of the Solar Spectrum (Philosophical Transactions).

paper prepared as above, was exposed to the spectrum, and washed with a solution too weak fully to excite it, two contrary actions were produced by the rays above and below the zero point or mean yellow. By the former the paper was bleached, the action beginning in the least refrangible violet, and extending upwards a considerable distance, and downwards to the circumference of a semicircle, having the point at which the action commenced for a centre. By the latter the paper was darkened, the blackness spreading upwards and downwards; upwards, till it passed the zero point, and nearly or quite attained the semicircle above-mentioned; and downwards to a space beyond the extreme red ray. By repeatedly washing the paper with the iodine solution, both actions grew more intense, but the bleaching action the most so. At length, by repeated washings the darkness produced at the lower part of the spectrum, began to give way, and was slowly replaced by a very feeble bleaching, which at length extended very far indeed below the extreme red rays, and upwards to join the semicircle c. Within this semicircle



and its train, a somewhat dark, perfectly circular and well defined solar image arose, its diameter being somewhat less than that of the semicircular terminations, so as to leave a perfectly clear and distinct white border all around it, as represented in No. 2. This circle gradually extended

itself into an oval or tailed form, but preserving its circular shape below, and maintaining the white border inviolate. Finally, after long-continued action, the interior browned oval above-mentioned, was found to have been prolonged into a figure of the annexed form, of which the termina-



tion by a narrow neck and circular enlargement, indicates the definite action of a ray much further removed along the axis of the spectrum.

(157.) We shall perceive from this, that four distinct actions are exerted on these papers:—1st, Bleaching by the most refrangible rays; 2ndly, Blackening by the least refrangible; 3rdly, Darkening by the most refracted portion of the spectrum, after the first bleaching has been continued for some time; and, 4thly, Bleaching by the rays of least refraction, which in the first case produced an exaltation of the dark colour. The two last actions may be imitated to a considerable extent by radiant heat; and I have but little doubt that the bleaching by the red rays is due to thermic influence. The two first actions, it will be evident, are, first, the formation of the iodide of silver; and, secondly, the oxidation of this iodide. The definite spaces to which the rays are confined, on which these actions depend, are very remarkable, and appear to point to an involved system of solar emanations, which we are not in a situation at present to explain.

(158.) These very peculiar influences may be prettily illustrated by placing a piece of the prepared paper, with an engraving superposed, behind four pieces of coloured glass. Beneath a blue glass the engraving will be very perfectly copied, as a positive picture, with correct light and shadow. If a deep green glass is used, a negative picture will result from the blackening of the paper under those parts which are white admitting the most light, and

the same takes place under a yellow glass; but under a glass stained red with oxide of gold, a negative picture is formed, not by the darkening of the oxide of silver, but by the eating out of *strong lights* on all the lines which correspond with the *dark parts* of the engraving, these parts having the most calorific influence.

(159.) Experience has convinced me, that the use of coloured glasses, in any experiment which has for its object the elucidation of any of the phenomena connected with the chemical power of the sun's rays, is to be avoided, as leading to error in many cases, and giving uncertain results in all. No correct conclusions can be arrived at in any way, but by prismatic analysis. The above, and some other experiments, which are to be found in these pages, are only given as an easy way of showing some of the very peculiar and beautiful phenomena with which the art of photography has made us acquainted. I shall, in a future page, make some remarks on the influence of coloured media, when I shall endeavour to show the numerous sources of error to which we are liable, when we trust *solely* to their use, however carefully they may have been analysed by the prism.

(160.) IODIDE OF SILVER ON METAL PLATES. — If upon a plate of polished silver we place a small piece of iodine, and apply the heat of a spirit-lamp or candle beneath the plate for a moment, a system of rings is speedily formed, which is somewhat remarkable. The first ring formed, which, spreading constantly, forms the exterior of the circle, is of a bright yellow colour; within this there arise successively rings of green, red, and blue colours, and then again a fine yellow circle, centered by a grayish spot on the place occupied by the iodine. On exposing these to sunshine, it will be found that the outer yellow circle almost instantly changes colour, and that the others slowly change in the order of their positions, whilst the interior yellow circle resists for a long time the solar influence. These rings must be regarded as films of the

iodide of silver, varying, not only in thickness, but in the more or less perfect states of combination in which the iodine and the metal are. The exterior circle is an iodide, in an exceedingly loose state of chemical agregation: the attractive forces increase as we proceed towards the centre; where a well formed iodide is formed, which is acted upon slowly by sunlight. The exterior and most sensitive film constitutes the best surface for the Daguerreotype plates. The changes which these coloured rings undergo are remarkable; by a few minutes' exposure to sunlight, an inversion of nearly all the colours takes place, the two first rings becoming a deep olive green and a deep blue inclining to black. It is a very pleasing experiment to form those beautiful rings by placing a small piece of iodine on a little silver leaf, and then, covering one half of them with an opaque body, expose them to the solar rays.

(161.) THE DAGUERRETYPE. — The material used as the tablet upon which the solar radiations are made to impress external nature, in this process is copper, plated with silver. The copper serves principally to support the silver; but it has been stated, with some degree of correctness, that the combination of the two metals tends to the improvement of the effect. It is essential to success that the silver should be brought up to the most perfect polish. This is best done by polishing with cotton dipped in sweet oil, and finely levigated Tripoli powder or rotten stone. The cotton is to be frequently changed, and great care must be taken that the plate is not touched by the fingers. Dry cotton and very fine Tripoli dust must be used to complete this part of the process. The plate is then subjected to the heat of a spirit-lamp or a charcoal fire, for a few minutes, and cooled as speedily as possible, by placing it on a mass of metal or a stone floor; the object of this is to remove the organic film which the oil has left on the plate. Daguerre has stated it as the result of his experience, that any organic or atmospheric film

interferes with the rapidity of the operation ; hence, after having polished the plate, he floats it with pure water, and heats it to a high degree over a spirit-lamp, and afterwards pours off this layer of water in such a manner that its surface, on which the film, or any sediment removed, may float, shall not touch the plate ; after this, the plate is not again polished. This film has been stated by some to assist in the formation of the images ; but experience has shown, that too much attention cannot be bestowed on its removal. The plate, when cold, should be finished off with cotton dipped in a solution of one part of nitric acid to sixteen of water, then with dry and clean cotton, and lastly rubbed upon a velvet buffer.

(162.) The next operation is to form on the surface of the silver the sensitive film. On the success, or otherwise, of this operation every thing depends. The plate, when viewed by a weak artificial light, should present a perfectly yellow and brilliant surface. Several plans have been suggested, by which the iodine may be made to attack the plate equally ; but all of them require, on the part of the operator, the closest care and attention. The simplest method is to place in the bottom of a box pieces of iodine, and cover them with a piece of gauze stretched on a frame which fits the box. The polished plate is placed a short distance above the gauze. The cover of the box being closed, all is allowed to remain in this state for two or three minutes, when, on removing the plate, it will generally be found that the required fine yellow surface is produced.

(163.) Mr. Goddard in 1840, and M. Claudet in 1841, succeeded in quickening the sensibility of these plates, by combining bromine or chlorine with the iodine. This is effected in various ways by different operators, the usual method being to iodize the plate in the first instance, and then to expose it to the vapour of bromine, or its combination with chlorine or iodine. (Various preparations are sold as accelerating agents, all of them being some preparation

of bromine.) The result is the conversion of the yellow iodide of silver into a rose-coloured surface, which we may regard as a bromo-iodide. When the plate is properly prepared in this manner, an extreme degree of sensibility is the result. The original process of Daguerre occupied from 15 to 20 minutes in the production of a picture; but by the method now employed, a second or two, in the ordinary conditions of sunshine, prove sufficient for the production of portraits in the camera obscura.

It is not necessary that the plate should be used as soon as it is excited, some of our most practised Daguerreotype artists preferring to use a plate which has been prepared for some hours, to one taken directly from the iodizing operation.

(164.) The prepared plate is now placed in the dark chamber of the camera obscura; and being properly adjusted, it is exposed to the agency which is to impress upon it the required images. The length of time necessary for the production of the best effect, varies with the state of illumination, the kind of image to be copied, the condition of the plate, and other things which can only be arrived at by experience. In general, where the plate is prepared, as directed by Daguerre, with the iodine alone, about five minutes is required in ordinary sunshine, to copy any architectural pile; but a much less time is sufficient where bromine is added.

(165.) The plate being removed from the camera obscura, no image should be visible upon it. A change has taken place; but as the colour of the plate is not altered, that change cannot be seen. If the plate in any part is browned by too long an exposure, the lights of the picture are injured. To develop the hidden picture, the plate is placed in a box, at the bottom of which is a little mercury, so arranged that the heat of a spirit-lamp may be applied until the temperature of the mercury is about  $167^{\circ}$  Fahr. The lamp is then removed; and the plate, which is watched through a glass in the side of the box, by the light of a



taper, allowed to remain until the picture, in all the beauty of its minute details, is perfectly brought out. It is then removed; and it has to be subjected to the operation of fixing, or of rendering the plate of metal insensible to any further solar agency.

(166.) In forming a Daguerreotype image, it is not absolutely necessary to warm the mercury. Faraday proved that mercury was volatilised at common temperatures; and Moser has pointed out, that if the Daguerreotype plate, after it is taken from the camera, is placed over a vessel of cold mercury for some hours, the image will be brought out in the same manner as if the mercury had been warmed. Moser has likewise shown, that if the mercurial vapour is raised to a temperature between  $250^{\circ}$  and  $300^{\circ}$  Fahr., the Daguerreotype picture becomes fixed, and may be strongly rubbed. "It loses a little of its intensity at first, but not afterwards. The images, however, cannot generally resist rubbing with moist materials, as with polishing substances." It is not necessary to have recourse to the ordinary methods for removing the iodine from these fixed pictures, as it can be rubbed off.

(167.) Various theories have been from time to time put forth, on the action of mercury on the silver after it has received its impression by radiant action. The Rev. W. Fowler Kingsley has stated his views in a recent communication on this subject, from which I quote:—

"The image of the object to be delineated is now formed upon the plate, and then the plate is exposed in the dark to the action of the fumes of mercury, which in a short time whiten the parts that the light has acted on. It used to be thought that the image was formed by particles of mercury being deposited upon the surface of the silver. This, however, I am sure is quite a mistake; and though I am unable to explain the whole action that takes place, I have no doubt of the nature of it. The vapour of mercury has a decided affinity for

oxygen, iodine, bromine, and chlorine; when, therefore, the plate is exposed to it, the vapour deprives the iodide of silver of its iodine, and deposits pure silver. When bromine and chlorine are also present, silver is reduced, and at the same time salts of mercury are formed; and I have no doubt that the different colours of the lights, according to the different proportions of iodine, bromine, &c., are due to these salts of mercury; but as the quantity is very minute, it is a matter of great difficulty to detect them,—calomel and the black oxide I have detected. After the plate has been acted upon by the mercury, it is fixed by first removing the unreduced iodide by a bath of hyposulphite of soda, and then by gilding it slightly with hyposulphite of gold. If the action of the light be too strong, metallic silver is formed at once, and then the mercury unites with it, and forms an amalgam that is not as light in colour as the silver reduced in the first instance. This seems to be one of the points where there is hope of gaining by further experiments; for if some way of reviving the silver on those parts of the plate where the light has not actually reduced the silver, can be discovered, without destroying the revived parts, we should be able to make sure of every plate by merely giving time enough to the exposure to the light. I may mention that the vapour of aldehyde gives promise of effecting this object. As a de-oxidizing or de-iodizing agent, it is most powerful, but the difficulty it to restrain its action."

Mr. Kingsley has contributed so much that is of value in the applications of Photography to the microscope, &c., that all his remarks must have considerable value. I cannot but think however, had he tried a few experiments on the deposition of vapours on bodies acted upon by either *Heat* or *Light*, where chemical change was out of the question, as on polished metal plates or glass, he would have modified his remarks. I am perfectly satisfied that Mr. Kingsley is wrong; the phenomena are far less complicated than is usually imagined; and he, indeed, in

one of his later paragraphs in the same paper, indicates, without knowing it, the true action.

The bromo-iodide, or iodide of silver, when exposed to radiant action, is immediately decomposed into metallic silver, and the iodine or bromine liberated attacks the surface of the plate, beneath the sensitive film. Now, the amount of decomposition,—that is, the quantity of silver which is left on the surface in a finely divided metallic state,—bears an exact relation to the amount of radiant force which has been acting along certain lines. The vaporized mercury immediately unites and forms an amalgam with this silver; and thus are formed the high lights and middle tints of a Daguerreotype picture. If the iodine, which is then combined with the under surface of silver, is allowed to attack the mercury, a very poor result will be obtained; hence the advantage of immediately removing the iodide of silver by the fixing agent employed.

(168.) Fixing may be effected in several ways, all of which depend upon the removal of the iodine from the plate. A strong solution of common salt will do this; but if the plate is placed in such a solution, and then touched with a rod of zinc, the removal is much more rapidly and effectually accomplished. By far the best plan, however, appears to be that recommended by Daguerre in the first instance. The plate is first placed in clean cold water, and then into a solution of the hyposulphite of soda, in which it is moved to and fro, until all the yellow colour is completely gone. It is then removed, placed in an inclined position, and boiled rain water, cooled so as to be just warm, poured over the plate in a continuous stream. Any drops of water which may remain on the plate, must be removed by forcibly blowing over it. The process is now completed, as far as preventing the further action of Light is concerned. The picture is formed of the finely divided silver, amalgamated with the mercury deposited over those parts on which the che-

mical change has been effected, represented by the high black polished face of the silver.

(169.) This picture can, of course, be immediately destroyed by a touch; it is, therefore, necessary to protect it at once, by a glass or some other means. Berard, Fizeau, and others, have recommended the use of the chloride of gold, for the purpose of giving adhesion to the mercurial amalgam. It is thus applied, according to the method recommended by M. Fizeau, and which appears to have been the most successful of any of the plans which have been adopted. A double salt of hyposulphite of soda and gold is formed, by mixing very dilute solutions of the respective salts. After the iodine has been removed, as before directed, the plate is placed in an iron frame, and a sufficient quantity of the solution of salt of gold to cover the plate, poured over it. It is then heated by a spirit-lamp for a minute, or until the impression acquires the greatest strength. The liquid is then poured off, the plate well washed and dried. Gold is deposited over the plate, and thus the picture rendered less liable to injury.

Dr. Berres of Vienna, states that considerable success has attended his plan, which consists in exposing the plate for a few minutes to nitric acid vapour, and then placing it in nitric acid, at  $61\frac{1}{4}^{\circ}$  Fahrenheit, in which a considerable quantity of silver and copper is dissolved. Shortly after being placed therein, a precipitate of metal is formed over the photograph. It is then removed, and the plate polished with chalk or magnesia, until the picture can be clearly seen.

(170.) The power of multiplying these very beautiful productions is much to be desired. Several plans have been proposed and used by the inventors, with certain degrees of success, particularly Professor Grove's method of etching by electrical agency. All of them, however, are of great uncertainty; and even with the most careful manipulation, a successful result cannot be depended on. It does not form a part of the plan of the present work to

embrace these matters, though they are of the highest interest to every one who is concerned in the success of photographic publication. It must, however, be acknowledged, that the only successful method of multiplying original photographic designs, appears to be the use of processes on paper, or some more transparent material which, giving negative pictures in the first instance, will afford positive copies.

(171.) As long back as 1841, it was announced that M. Daguerre had discovered a process by which an instantaneous effect was produced; and in a communication with which the author was favoured from Daguerre himself, he states, "*By means of that new process it shall be possible to fix the images of objects in motion, such as public ceremonies, market-places covered with people, cattle,*" &c. But some great obstacle appears to have interfered with the successful practical use of this new and important discovery. Daguerre's attempts to improve the process which bears his name, were all of the most complex nature; and his processes singularly unscientific.

(172.) The expense of metallic plates and their inconvenience, particularly to travellers, render it very desirable that some material, such as paper, might be employed instead of them. Some very tolerable effects have been produced upon silvered paper; but the pictures thus formed, want the fine black surface, which is to contrast with the mercurial vapour, and which forms the chief charm of a good Daguerreotype. In the Philosophical Transactions, Part II. for 1840, is a paper, by the author, "*On the Influence of Iodine in rendering several Argentine Compounds spread on Paper, sensitive to Light.*" As many of the results are of considerable importance, particularly as they bear upon some of the opinions which we shall have to examine, I shall briefly mention such facts as appear necessary to the complete elucidation of this very interesting subject.

(173.) Any of the ordinary photographic papers will

darken, by exposure, to a brown or dark olive colour. Exposed to the vapour of iodine, the paper becomes of a steel blue or violet colour. If subjected to solar influence in this state, mercurial vapour attacks all the parts on which the Light has acted, in the same manner as it does the iodized metallic plate, giving a tolerable picture. I also found, that perfectly pure oxide of silver, spread on paper and iodized, was similarly disposed to receive the mercurial vapour, after it had been submitted to the sun's rays. The yellow-brown phosphate of silver was found also to acquire additional sensitiveness under the influence of iodine, and to yield a tolerable picture when exposed to the mercurial fumes.

(174.) Papers which were prepared by first saturating them with strong solutions of the nitrate of silver, and then exposure to phosphuretted hydrogen gas, until there was a complete revival of the silver over the surface of the paper, were found to be acted upon by iodine, in a similar way to the silver plates themselves, and for most purposes are capable of being substituted for them. The pictures, when the papers are well prepared, are formed as readily as upon the iodized plates, and are not at all wanting in the beauty of their general effect, or in the delicacy of their minute detail. It unfortunately happens that a considerable degree of risk attends the preparation of the paper by this spontaneously inflammable gas.

(175.) Papers prepared in a similar way, substituting the sulphuretted for the phosphuretted hydrogen, are in nearly all respects equal to them. Some difficulties attend the preparation; but by observing the following directions, papers of a very uniform dark gray surface may be prepared:—The paper is first soaked in a solution of the hydrochloride of ammonia, carefully wiped with cotton cloths, and then dried. It is next dipped in a solution of nitrate of silver, dried in the dark, and then carried into a vessel in which sulphuretted hydrogen is slowly forming. When it has darkened to an iron brown, the paper must be

passed through water slightly impregnated with chlorine or muriatic acid, and again dried. It is once more dipped into an argentine solution; and when dry, subjected a second time to sulphuration. These papers are best iodized by drawing them slowly over a saturated solution of any salt of iodine in which is dissolved a considerable quantity of iodine; care must be taken that one side only of the paper is wetted. It is then dried near the fire, and subjected in the camera to the solar agency. After mercurialisation, the picture is fixed most effectually by a strong solution of common salt used moderately warm.

(176.) If when these drawings are finished, they are placed in a solution of corrosive sublimate, the images entirely disappear; but after a few minutes they are seen, as if by magic, unfolding themselves, and gradually becoming far more beautiful than before; delicate lines, at first invisible or barely seen, are now distinctly marked, and a rare and singular perfection of detail is given to the photograph. A singular obliteration is described before (94.); but in this case the results are very different, the picture being again restored by the agent which caused it to disappear. It would appear that the mercury on the paper is slowly converted into a protochloride; the *modus operandi* is not, however, quite evident.

(177.) From the great interest which attaches to the discovery of Daguerre, we must now endeavour to examine some of the most remarkable points in the phenomena which are afforded in pursuing his photographic practice. If we expose a prepared plate, for a considerable time, to the action of the chemical radiations in the camera, it is darkness and a *negative* picture results. The discovery of Daguerre is that, before the negative image is formed so as to be visible, the iodide of silver has undergone a change, which has given it the property of condensing over well defined spaces the vapours of mercury. It has been shown by M. E. Becqu  rel, that if the plate be removed from the camera, before it has been exposed suf-

ficiently long to afford a visible picture, or at least anything beyond the faintest outline of an image, the process may be *continued* by exposing the plate to sunshine under a *red glass*. E. Becquérel assumes, from these results, that there exists two orders of rays, which have not been previously described, and which he calls

*Rayons excitateurs*, and

*Rayons continuators*.

(178.) It will be found, when we come to an examination of the subject in all its details, that the process, supposed to be carried on by the *rayons continuator*, considering them as a new class, is probably due to the calorific rays, and that very nearly the same effect is produced by the application of artificial heat to the under surface of the plate. But it is not entirely to the calorific rays that the effect is due. We know, that the least refrangible rays of the prismatic spectrum are not without some chemical power, and that this is a power quite independent of their heating effect; and it will be found, with nearly all the sensitive preparations, that the action, under any circumstances of sunshine, is carried on much more rapidly upon those parts over which a chemical disturbance has been already begun, than over the other parts. Moser, indeed, admits that some blue and violet rays penetrated the red glasses he used in his experiments, therefore the only effect which, as I conceive it, the red medium produced, was to retard the change, over the undisturbed parts of the plate, whilst a sufficient quantity of the most refrangible, and extra spectral chemical rays, had passed the glass, to continue the change which had been already begun. Yellow glasses were found by Moser to produce, first negative and then positive images; but "*these positive images have always a blackish covering*." Now this is as easily explained as the action of the red glass. The change is carried on "*by the large quantity of white light*" which these yellow glasses allowed to pass, with much greater rapidity over the parts on which the chemical rays



have already acted, than on the others, which were, however, gradually changed. Any one conversant with the ordinary photographic processes, must have observed, that when the maximum point of darkening has been arrived at, a peculiar olive tinge gradually comes on\*, and the picture being now a fine brown colour on an olive ground may be considered a positive one.

(179.) What is the nature of the change which the iodide of silver undergoes on these Daguerreotype plates? This question has been often asked, and answered in various ways. Draper†, from an experiment in which he placed a paper saturated with starch on an iodized plate, and which, after exposure, gave no evidence of the formation of the iodide of starch, from the liberation of the iodine, infers that no decomposition of the sensitive surface has taken place. Moser contends, that "the action of Light does not necessarily consist in the separation of two chemically combined bodies." He appears to attribute the alteration of colour, to an isomeric change in the iodide of silver.

(180.) It will be found, if we allow one part of a sensitive plate to blacken, whilst the other portion is protected from action, that the dark part is very easily removed by rubbing with the hand, whilst the unchanged division, resists any such mechanical means of removal. In the very fine powder thus rubbed from the silver, I have never been enabled to detect any iodine, but it comports itself, in all respects, like the finely divided metal. A fact mentioned by Moser—viz. that he has been enabled to remove film after film of the sensitive surface, and yet had a surface which was still sensitive to Light, which he considers conclusive in favour of his argument, that the combination of silver and iodine is not

\* Moser says, "I exposed iodized plates to daylight, and whenever possible to strong sunlight. *The plates became first black, then lighter, and lastly greenish.*"

† Philos. Mag., Sept. 1841.

decomposed—appears to me to prove my position, that as the iodide is liberated from the surface, it attacks the layer of silver below it, and, according to the length of time during which the action of the solar rays may be continued, the greater the quantity of silver which is left decomposed on the surface, and the greater the depth of abrasion into the plate. The iodine may attack the plate to a considerably greater depth than we imagine; and hence, although we may remove eight surfaces, we may still have a sensitive surface left. The powerful affinity of this element for the metals, will countenance this opinion, and it will account for the failure of Dr. Draper to produce the iodide of starch in his experiment. It has been shown by M. Lerebour, that the presence of the smallest quantity of iodine vapour in the camera is quite sufficient to prevent the formation of any image; and he distinctly states that he has failed to produce a picture, during the whole of a long summer day, owing to his having kept his iodizing box and camera together, by which the latter received a little of the vapour of this subtle elementary body. Ammonia dissolves off from the plate the darkened portion, whilst a solution of the muriate of soda, or of the hyposulphite of soda, removes the unchanged iodide. These facts certainly support the view, that decomposition has taken place on the sensitive surface, that the iodine has been liberated by the action of the solar rays, and that this change fits parts of the plate for the condensation and combination of the mercurial vapour. There are some facts, however, curiously connected with this action of vapours, which will hereafter claim our attention. Mr. George Shaw has proved that a Daguerreotype plate may be exposed to strong light, and yet immediately restored to its original condition of sensibility by the most transient exposure to the vapour of iodine. See *Philosophical Magazine*.

(181.) *Prismatic Analysis*. — In the *Philosophical Magazine* for April, 1840, the author published an ac-

count of the effects produced by the spectrum on a Daguerreotype plate. The experiments have been repeatedly tried, and the results have been the same, if we except a little shifting of the point of maximum action. The most refrangible portion of the spectrum appears, after the plate has been exposed to the vapour of mercury, to have impressed its colour; the light and delicate film of mercury which covers that portion, assuming a fine blue tint about the central parts, which are gradually shaded off into a pale grey; and this is again surrounded by a very delicate rose hue, which is lost in a band of a pure white. Beyond this, a protecting influence is powerfully exerted; and, notwithstanding the action of the dispersed light, which is very evident over the plate, a line is left, perfectly free from mercurial deposit, and which, consequently, when viewed by a side light, appears quite dark. The green rays are represented by a line considerably less in size than the luminous green rays. The yellow rays appear to be without action, or to act negatively, the space upon which they fall not receiving the mercurial vapour; and it consequently is seen as a dark band. A white line marks the place of the orange rays. The red rays affect the sensitive surface in a peculiar manner; and we have the mercurial vapour, assuming a molecular arrangement which gives to it a fine rose hue; this tint is surrounded by a line of white vapour, shaded at the lowest extremity with a very soft green. Over the space occupied by the extreme red rays, a protecting influence is again exerted; the space is retained free from mercurial powder. It is not a little remarkable that a protected band is found to surround the whole of the least refrangible rays, and to unite itself with the band which surrounds the rays of greatest refrangibility; it is not equally well defined throughout its whole extent, being most evident from the extreme red to the green; it fades in passing through the blue, and increases again, as it leaves the indigo, until beyond the most refrangible rays it is nearly as strong

as it is at the calorific end of the spectrum. By *lightly rubbing* a Daguerreotype image of the prismatic rays, it is obliterated, except over the spaces corresponding with the yellow and red rays. In November, 1842, Dr. Draper forwarded to Sir John Herschel, a specimen of a Daguerreotyped impression of the solar spectrum, obtained by him in the south of Virginia; and in the Philosophical Magazine for February, 1843, Sir John Herschel published an account of his examination of it. In its principal features, this spectrum corresponds with those I have obtained; and I am inclined to attribute the variations which do exist, not merely to a difference in the Light of the sun, but also to some peculiarities in the prisms employed. I am quite inclined, with Dr. Draper, to believe that spectra obtained near to, or at a distance from the equator, will be found to vary considerably. The principal difference which is to be observed between Dr. Draper's spectrum on the Daguerreotype plate, and that which I have described, consists in the remarkable distinctness of the compartments, which are found between the space occupied by the yellow ray and the most refrangible portion of the spectrum. The same protected spaces are observed at the top and bottom of the spectrum; but there is no appearance of the same influence at the sides of the spectral image. Sir John Herschel has shown that the tints observed on this spectral image, are the Newtonian series of colours of the first order of the reflected rings; modified, however, in its first stages, by a cause which seems to have shifted the initial black of that series, to a higher point in the scale of thicknesses of the producing film, or to have displaced the whole series by the intrusion of a white commencement. For the Newtonian reflected tints of the first order are black; very feeble and hardly perceptible blue; brilliant white; yellow; orange, at which point the series breaks off. (*Herschel.*)

(182.) It will not be improper to mention here, that when copper, plated with silver cannot be procured, very

tolerable results may be obtained, by using plates of copper silvered, with the ordinary silvering compound of chloride of silver, common salt, and cream of tartar. The copper being brought to a perfect polish, is well washed with salt and water; a little of the silvering compound is briskly rubbed over the plate, until it presents a uniform coating of white silver; the plate is immediately washed in clean salt and water, and dried near the fire, by carefully rubbing it with very clean cloths. I have found that the polish of this silvering is much improved, by passing the plate through a very weak solution of iodine in water. A thin film of iodide of silver is thus formed. It is then exposed to sunshine, and afterwards rubbed with a clean leather and a little fine prepared chalk, by which the iodized surface is removed, and a beautifully polished face left to operate on. It is then again iodized, and used in the same manner as the plated copper tablets.

(183.) Some very curious results have been obtained by operating on silvered plates, coated with iodine in various ways. A silvered plate, with some leaves placed upon it and pressed close with a glass, was immersed in a solution of iodine in water containing iodide of potassium, and in this state exposed to the sunshine. An iodide of silver was rapidly formed, and blackened; this blackened coating was dissolved off, and another ensued. Thus successive layers of the salt were produced and removed, until at the expiration of an hour, all the silver was gone from the exposed parts of the plate. Upon removing the leaves, it was found that a most beautiful impression of them was made on the copper, *and they were of a rich green colour.*

(184.) A piece of glass was covered with silver leaf, and treated in the same way as the silvered copper. The metal was dissolved from the exposed parts, and a very perfect silver leaf left upon the glass.

(185.) It may be worthy of observation, that the image on the Daguerreotype plates may be completely obliterated by rubbing; but it may be again restored,

by placing it in a tolerably strong solution of iodine in water. I have often found that the parts over which the mercury has not been deposited are etched by the solution of iodine, and it does appear that, with some attention, a very important practical advantage may be taken of this remarkable peculiarity. The great difficulty lies in overcoming the spots which are formed by definite spaces in the metal, which are in different electrical conditions from the other parts. These form so many points of action, and give rise to circles, which rapidly spread and obliterate the design.

(186.) After exposure to Light, a well-prepared Daguerreotype plate was placed in a vessel in which chlorine was very slowly forming, from manganese and hydrochloric acid, and in a short time the iodized surface became perfectly black. In this state it was subjected to sunshine, the effect of which was to whiten the plate with much rapidity. My engagements did not allow of my following out this discovery; but in two or three trials which I made, very tolerable positive pictures were produced by the first process, without mercurialization.

(187.) BROMIDE OF SILVER.—This salt, like the iodide, does not appear to be very readily changed by the solar rays, when it is perfectly pure. The slightest admixture of the nitrate of silver renders it very susceptible of change, and under certain conditions it becomes the most sensitive of the photographic preparations. M. Biot has expressed it as his opinion that it is not possible to find any substance more sensitive to Light than the bromide of silver. This opinion must, however, be qualified by the above conditions. Sir John Herschel has used films of this salt precipitated upon glass plates, which, when dry, are washed over with a solution of the nitrate, with the greatest advantage, in the camera obscura. It must, however, be observed, with regard to this and other salts which are stated to be unchanged in their pure state, that this applies only to a visible change. We have distinct

evidence that a moment's exposure of the pure bromide of silver to the sun's rays is quite sufficient to produce a change, which may be rendered visible by the subsequent applications of agents having a powerful affinity for oxygen.

(188.) *Prismatic Analysis*.—As soon as the prismatic spectrum falls upon paper prepared with this salt, it blackens over the whole extent of action with nearly equal intensity. As far as I have been able to detect it, which it is difficult to do, from the rapidity of the action, the maximum effect is produced somewhere about the indigo ray. My own results correspond exactly with those obtained by Sir John Herschel, who says, "But the most characteristic peculiarity of the spectrum is its extravagant length. Instead of terminating at the fiducial point (the mean yellow ray) or thereabouts, the darkened portion extends down to the very extremity of the visible red rays. In tint it is pretty uniform (a grey black, not by any means intense) over the whole length, except that a slight fringe of redness (but no green or blue) is perceptible at the least refracted end." The author has, however, found that the grey-black may be very much darkened by allowing the nitrate of silver to be pretty much in excess; and by using a faint spectrum he has sometimes got decided evidences of natural colouration. Below the red ray an extended space is protected from the agency of the dispersed light, and its whiteness maintained; thus confirming the evidence of some chemical power in action, over a space beyond the luminous spectrum, which corresponds with the rays of the least refrangibility. In a subsequent chapter, devoted to the general consideration of all the conditions—particularly after the rays have been subjected to absorption—a still further examination of these salts of silver will be found.

(189.) *Photographic Application*.—If paper is first washed with a solution of the nitrate of silver (100 grains to an ounce of distilled water), and when dry with a

solution of 20 grains of the bromide of potassium in four drachms of water, a good bromine paper is prepared ; to render this sensitive, the silver solution is again applied. If used while yet wet, the paper is of exquisite sensibility, and may be used with advantage in the camera obscura. The advantages of the bromide of silver over every other salt which is usually employed, should lead to its general adoption, since all the least refrangible rays act on it with much greater energy than on either the iodide or chloride.

(190.) In 1841, I published a process, which I then considered as new, by which pictures were produced on bromidized papers, after an exposure of an exceedingly short duration. This process had, I afterwards found, been previously pointed out by M. Bayard : of this I was, however, quite ignorant. Although there are some objections to the process, it is so very interesting, as giving evidence of the rapidity with which faint solar radiations will effect a change of state, that it cannot be well omitted in this place.

(191.) Paper is prepared with bromide of potassium and nitrate of silver, in such proportions that the nitrate is in very slight excess. When used, it is washed over with a solution of 120 grains of nitrate of silver, and placed wet in the camera. After being exposed for a second or two, the screen must be closed, the camera carried into a dark room, and the paper allowed to dry in the dark. When dry, it is placed in the mercurial vapour box ; and heat being applied, the mercury is slowly vaporised. The picture now begins to develop itself, and gradually a most intense negative photograph results. It often happens that the picture appears at first clouded ; but if the paper is carefully placed in the dark, it generally, in the course of a few hours, gets clear. I have often procured most beautiful pictures by this method, after an exposure to solar influence for less than a second ; and even moving objects have been well defined,



showing the action to be almost instantaneous. Photographs thus obtained are best fixed by soaking the paper in a weak solution of salt in water, and then by brushing them over with the hyposulphite of soda. The great difficulty to be overcome in this process, is, the annoyance continually arising from the blackness produced over every part of the paper by the mercurial vapour. Often, when the best result appears to have been attained, in an instant the delightful picture vanishes away, and a sheet of blank blackness takes its place. It is not quite clear, to what this can be attributed; some kinds of paper are more liable to it than others, from which it would appear that it arises from the condition of the surface.

(192.) Bromide of silver may be used very advantageously with the gallic acid or the proto-sulphate of iron for the production of pictures. Since this salt is effected by those rays which exist in the least refrangible portion of the spectrum, I am inclined, under all circumstances, to regard the bromide as preferable to the iodide of silver. Certain it is that if we use either of these salts alone, or in a pure state, the bromide has an advantage over the iodide in sensibility, and all green or yellow objects are more perfectly copied on a paper prepared with bromine than on one in which iodine has been employed. Papers washed once with each of the following solutions—

Bromide of potassium 50 grains, water 1 oz.  
Nitrate of silver 100 grains, ditto—

may be used most advantageously for copying any fixed objects. They require but a few minutes' exposure, and at any time, the picture may be brought out, by washing with the solution of proto-sulphate of iron or gallic acid. These photographs, which possess all the requisites of good negative ones, may be well fixed, by washing with a weak solution of the bromide of potassium, or with the hyposulphite of soda.

(193.) If a paper is covered with a perfectly pure bromide of silver, it will, when washed over with a solu-

tion of the ferrocyanide of potassium, exhibit an increased degree of sensitiveness to solar agency; but the resulting picture, falls very short of that blackness which we get by using the iodide of silver, the darkest parts never becoming deeper, than a full grey or lead colour.

(194.) *Prismatic Analysis*. — If a bromidized paper, whilst under the influence of the spectrum, is washed with the ferrocyanide of potassium, it begins to darken instantly over the violet rays, which darkening action extends down to the edge of the red ray, some slight interference being observable about the region occupied by the yellow and orange rays. Then a bleaching action begins, over the space on which the red rays fall, which slowly extends up to the green: by a long-continued action, an oval spot begins again to darken, about the centre of the bleached space. In this case, as in that with the iodide of silver, if a second wash of the bromide of potassium is applied, the bleaching action is extended over the region of the most refrangible rays, and considerably beyond them. We observe again in this instance, the negative action of the extreme red rays, which has been previously described.

(195.) FLUORIDE OF SILVER. — The combinations of fluoric acid and silver were first examined by me in 1843, and particulars published in the first edition of this work in 1844. Sir John Herschel, indeed, suggested some experiments on glass plates of a very interesting description, but they do not appear to have been made, the object of which was to obtain at once etchings on the glass by the action of the liberated fluoric acid. Paper washed with fluoride of sodium, and then with nitrate of silver, is not more sensitive to Light than the nitrate itself, but it eventually becomes darker.

(196.) *Prismatic Analysis*. — A paper was washed first with nitrate of silver, and then with the fluoride of sodium. Under the spectrum the action commenced at the centre of the yellow ray, and rapidly proceeded upwards, arriving at its maximum in the blue ray. To the end of the

indigo the action was uniform; it then appeared to be very suddenly checked, and a brown tint was produced under the violet rays, all action ceasing a few lines beyond the luminous spectrum. Some faint indications of change were evident to the lowest edge of the yellow ray, but none whatever below that point. The colours of this spectrum are not a little remarkable when the paper is slightly browned by diffused light previously to its being exposed to the action of the spectrum. The following order of colours soon becomes evident: a yellow line distinctly marks the space occupied by the yellow ray, and a green band the space of the green: through the blue and indigo region the colour is an intense blue, and over the violet a ruddy brown—these colours are tolerably permanent.

(197.) The fluorides of sodium and of potassium have been used in many different manners, and variously combined. It has been found that the fluoride of sodium has the property of quickening the sensibility of bromidized papers to a very remarkable extent; and from this quality a new process, which I would distinguish by the name of the Fluorotype, resulted.

(198.) The Fluorotype.—This process, which is characterised by its easy manipulation, and by the sensibility of the papers when they are carefully prepared, consists in the formation of a salt of silver, which I suppose must be considered as a fluo-bromide of silver. It is somewhat difficult to say, which is the most efficacious manner of proceeding; but the difference, as it regards the sensibility of papers, is so very trifling, that this is not of much consequence. The paper may be washed first, with the bromide of potassium, and then with the fluoride of sodium; or, which will be found on the whole the best plan, the two salts may be united. The strength of the solutions should be as follows:—

{ Bromide of potassium	-	20 grains.
{ Distilled water	-	1 fluid ounce.
{ Fluoride of sodium	-	5 grains.
{ Distilled water	-	1 fluid ounce.

Mix a small quantity of these solutions together when the papers are to be prepared, and wash the paper once over with the mixture, and when dry, apply nitrate of silver, in solution, 60 grains to an ounce of distilled water. These papers appear to keep for some weeks without injury, and they become impressed with good images in half a minute in the camera. This impression is not sufficiently strong to serve, in the state in which it is taken from the camera, for producing positive pictures, but it may be rendered so, by a subsequent developing process.

(199.) The photograph is first soaked in water for a few minutes; it is then placed upon a slab of porcelain or stone, and a weak solution of the protosulphate of iron applied, which very readily darkens, all the parts on which the light has acted, to a deep brown, every object being brought out with great sharpness. When the best effect is produced the process must be stopped, or the lights suffer. All that is necessary is to soak the paper in water, and then fix the drawing with hyposulphite of soda. This process admits of numerous modifications.

(200.) PHOSPHATE OF SILVER was first suggested as a good photographic material by Dr. Fyfe, who recommends that the paper should be soaked in a solution of phosphate of soda, and then dried; after which the nitrate of silver is spread over one side of the paper by a brush; the paper is again dried, and afterwards put through the phosphate, by which any excess of nitrate of silver is converted into a phosphate. Although papers thus prepared answer exceedingly well for copying by application, they do not change so readily as to render them of any use in the camera obscura. One advantage possessed by these phosphated papers, is the readiness with which they are fixed by the application of a weak solution of ammonia. The yellow phosphate of silver is quite soluble in ammonia, and we are thus enabled to remove it very readily, without doing much injury to the darkened parts of the paper. Dr. Fyfe recommended the application of the precipitated

phosphate to paper, glass, or metal, in the form of a paint; and if this is carefully done, some very pleasing effects are to be produced. After the phosphate has been darkened by exposure to sunshine, it is very readily bleached by the joint agency of the solar rays and the iodide of potassium. This was the process published by Dr. Fyfe, for producing positive photographs by one application, at a very early period; other processes were found, however, to give much more satisfactory results, and it is now but seldom used.

(201.) *Prismatic Analysis*.—The spectral image formed on the phosphate, does not present any thing very remarkable. The maximum point is situated in the mean blue ray; the chemical disturbance is carried on actively over the indigo, with some energy in the violet rays, and to a considerable distance beyond the visible spectrum. It extends downwards, nearly to the centre of the yellow ray: about this region the image has a decided green shade. A space without any visible change here presents itself, but over the region occupied by the red rays, the phosphate assumes a brick-red colour. A precipitate, consisting of phosphate of lime, combined with organic matter, common salt, and nitrate of silver, was used by Sir John Herschel, and the image of the spectrum obtained upon this preparation appears very nearly to have resembled that just described. Some trifling differences are observed; but these are merely the shifting of the points of maximum effect which are constantly varying with the dose of the ingredients.

(202.) *TARTRATE OF SILVER*.—This salt, whether prepared from pure tartaric acid, from the tartrate of potash, cream of tartar (*bitartrate*), or from Rochelle salt (*tartrate of potash and soda*), appears at first to change, but very slowly, under the influence of solar radiations; but after a short period the darkening process is very much accelerated, and the paper prepared with this salt assumes a much higher degree of blackness than almost any other

of the argentine preparations. For copying engravings, or botanical specimens, it possesses some advantages; but I have never found any combination of the tartrates and the salts of silver, sufficiently sensitive for use in the camera obscura.

(203.) *Prismatic Analysis*.—The results obtained by Sir John Herschel are so very curious, that I shall take the liberty of transcribing his own words. The kind of paper employed by this distinguished philosopher was thus prepared:—“1st, Nitrate of silver, S.G. 1·132; 2d, Saturated solution of Rochelle salt; 3d, Nitrate of silver, 1·132; which proving but little sensitive, a third wash of the nitrate was added, by which its sensibility was materially increased, its other qualities remaining unaffected. The spectrum impressed upon this paper commenced at, or a very little below, the mean yellow ray, of a delicate lead colour, but faint and dilute; and when the action was arrested, soon after the first impression was made, such was the character of the whole photographic spectrum. But if the Light was allowed to continue its action, there was observed to come on suddenly a new and much more intense impression of darkness, confined in length to the blue and violet rays; and, what is more remarkable, confined also in breadth to the middle of the sun's image, so far, at least, as to leave a border of the lead-coloured spectrum traceable, not only round the clear and well-defined convexity of the dark interior spectrum at the least refrangible end, but also laterally along both its edges. And this border was the more easily traced, and the less liable to be mistaken, by reason of its singular contrast of colour with the interior spectrum. That of the former, as was observed above, was lead grey: of the latter, an extremely rich, deep, velvety brown. The less refrangible end of this interior brown spectrum, presented a sharply terminated and regular elliptic contour, the more refrangible a less decided one.” Sir John Herschel discovers three points of maximum intensity in this spectrum, situated

about the least refrangible blue, the most refrangible indigo, and beyond the visible rays. In my note-book I have marked but two maximum points—one situated in the indigo ray, and the other at the edge of the most refrangible violet rays. Having attempted to explain some effects which I observed upon Daguerreotype plates, nearly corresponding with those just described, by a speculation similar in its general character to that of this experimentalist, whose ideas on this subject I was not at all aware of until after the publication of my own, I shall again copy into my pages Sir John Herschel's own words:—

(204.) “It may seem too hazardous to look for the cause of this very singular phenomenon, in a real difference between the chemical agencies of those rays which issue from the central portion of the sun's disc, and those which, emanating from its borders, have undergone the absorptive action of a much greater depth of its atmosphere; and yet I confess myself somewhat at a loss what other cause to assign for it. It must suffice, however, to have thrown out the hint; remarking only, that I have other, and, I am disposed to think, decisive evidence, of the existence of an absorptive solar atmosphere, extending beyond the luminous one. The breadth of the border, I should observe, is small, not exceeding 0·5 or  $\frac{1}{4}$ th part of the sun's radius; and this, from the circumstance of the experiment, must necessarily err in excess.”

(205.) If paper, prepared with tartrate of silver, is allowed to darken slightly, and then washed over with a weak solution of the iodide of potassium, the darkening process proceeds with great rapidity, and a most intense blackness results.

(206.) If a paper prepared with the tartrate of silver as above is washed over, before exposure even, with a solution of the iodide of potassium, its sensibility is very much increased; and we find, by exposing such a paper to the prismatic spectrum, that a very different image is impressed. The impression does not descend below the green

ray of the spectrum, but at that point a delicate blue or grey colour is impressed; it rapidly darkens, and throughout the whole of the most refrangible rays a very intense blackness is produced, which penetrates deeply into the paper. The darkening process is carried for a very considerable space beyond the last visible violet ray, but with a very diminished intensity. The least refrangible rays do not appear to act at all; or if at all, they assist in converting the whole of the tartrate into iodide of silver. We do not find any of those protected spaces in this spectrum which are observed in the photographic image received on the pure tartrate of silver.

(207.) If the same paper is washed with the ferrocyanide of potassium, its sensibility is also improved. The impressed spectrum, in this instance, exhibits the maximum effect about the blue and indigo rays; but it is prolonged through the mean yellow, down to even below the least refrangible red ray, though it is not extended so far beyond the visible violet.

(208.) It would only be unnecessarily complicating the subject, and swelling the size of this volume, if I particularised the effects produced upon all the salts of silver which I have examined. Those already described may be regarded as types of the others. The carbonate, sulphate, acetate, citrate, and oxalate of silver, all undergo a considerable, and a tolerably rapid change, under the influence of sunshine. In some proportions the oxalate exhibits a very high degree of susceptibility; and with this salt, the citrate, and the acetate, the same double and triple maxima of intensity occur, when they are subjected to prismatic influence, as we have seen occurs with the tartrate.

(209.) BENZOATE OF THE OXIDE OF SILVER. — Although I have passed over many of the salts of silver, without particularising the effects produced, I cannot refrain from calling attention to some few of the organic combinations. The Benzoates dissolve pretty freely in warm water, and a single wash with their solutions renders paper tolerably



sensitive. The pictures thus procured are fixed most readily by washing in warm water.

(210.) BENZOATE OF SILVER, precipitated from the nitrate of silver by benzoate of ammonia, redissolved in boiling water, and washed over good writing paper, renders it moderately sensitive. The first action is far from being energetic, under the greatest intensity of sunshine; but after a short time the grey tint which is at first formed, passes very rapidly into a beautiful deep brown. The benzoate of ammonia and the nitrate of silver in successive washes, has been repeatedly tried, but without having obtained any improvement in the result. Under this section I may place papers prepared with hydro-benzoinamide and nitrate of silver; with formobenzoate of silver, and the benzoate of hydruret of benzule and nitrate of silver, the results being very similar. It will be interesting, however, to describe the results of prismatic analysis upon two or three of these preparations.

(211.) *Prismatic Analysis.* — Benzoate of oxide of silver. The action of the prismatic spectrum is first evident in the mean blue ray, from which it slowly extends upwards in nearly uniform force to the upper edge of the indigo ray, beyond which it rapidly diminishes in intensity. *The space occupied by the invisible chemical rays is maintained, even during prolonged exposure, much whiter than those parts of the paper under the influence of the diffused light.* This is the first instance in which the most refrangible rays were observed to exercise the same kind of influence, as the least refrangible rays have been described as doing. Below the blue ray, the action extends to the lowest edge of the green ray, beneath which no evidence of change can be detected. Hence we have a spectral image, which is confined to a space but little more than one half the length of the luminous spectrum, if we except the portion occupied by the extra spectral violet rays.

(212.) Formobenzoate of silver. — The action of the

spectrum in this instance is also seen to begin about the region of the mean blue ray. It goes on with apparently equal energy down to the yellow rays, and is tolerably active to the upper edge of the orange rays. Washing with the hyposulphite of soda, however, shows a well-defined line of maximum intensity, which exactly corresponds with the least refrangible blue rays. Above the blue, the action is powerfully exerted through the indigo rays, after which it declines in energy, but it is continued beyond the visible violet, over a space quite equal in extent to that of the visible violet rays.

(213.) Benzoate of Hydruret of Benzule and Nitrate of Silver.—The chemical change on this preparation commences at the upper limits of the green, and reaches its maximum at a point corresponding with the mean blue ray, after which it gradually diminishes, and any visible effect ceases just beyond the most refrangible violet rays. The rays below the green appear to be quite inactive. This spectral impression is scarcely more than one half the length of the visible spectrum.

(214.) It has been before stated, that gallic acid had the power of calling forth the dormant images from these combinations of benzoine. I merely recur to this point to state, that it will be found, on washing over any of these papers with this acid, after they have been exposed to the spectrum, that evidences of decided action will be observed over the whole of the space covered by the prismatic image. These facts are, in the present state of our knowledge, exceedingly enigmatical; but it appears to me, that by recording them, we advance step by step towards the development of some important truth.

(215.) It might appear, from the very unstable character of the combinations of cyanogen, that combined with the salts of silver these would produce very susceptible photographic compounds. Such, however, is not generally the case. The pure cyanide of silver undergoes but little change during an exposure of many days. The

amazing sensitiveness imparted to the iodide of silver by the ferro-cyanide of potassium has been already spoken of. A weak solution of hydro-cyanic acid produces the same effect, but in a slighter degree.

(216.) If a solution of the red prussiate of potash is washed over nitrate of silver, we have a photographic compound of some interest. In about half an hour a very beautiful copy of a print may be taken. Over all the parts which correspond with the lights of the picture, Prussian blue is formed, which appears green when contrasted with the yellow of the paper. If a small portion of the protosulphate of iron is added, the blue produced is much more intense. This chemical change is, I find, brought about entirely by the blue and violet rays of the spectrum.

(217.) If chloride of silver is allowed to darken by exposure to sunshine, and is then washed over with a solution of the ferro-cyanide of potassium, no very evident action is visible. If, however, this paper is exposed under a deep green glass, it will be found to bleach with some degree of rapidity. If exposed to a very concentrated spectrum, this bleaching power appears to be exerted by the yellow and green rays, whereas over the other parts symptoms of darkening are sufficiently evident.

(218.) If by washing a paper, which has been saturated with nitrate of silver, with a solution of caustic potash, we cover it with an oxide of silver, or, still better, if, instead of potash, we use ammonia, and then wash it with hydrocyanic acid, the paper is, of course, bleached in the dark, and the resulting cyanide of the oxide is readily blackened by exposure to the solar rays. This shows how very slight a difference in the manipulatory processes will change the character of a compound in its relations to the solar rays.

(219.) Chromate of silver, arseniate of silver, and some other salts, have been described by chemists as absolutely unchangeable by the Sun's rays. Experience has, how-

ever, shown that this is not the case, as a very sensible change takes place, either after a short or long exposure, upon all the salts of silver yet examined. The chromate of silver does not change much in colour, even after an exposure to good sunshine for many days, but it eventually assumes a very metallic brown shade, and revived silver is readily detected. Under certain circumstances, the arseniate becomes really a very good photographic agent, and I find that paper washed with the *liquor arsenicalis* of the Pharmacopœia (a solution of arsenic in water, assisted by the presence of some potash), and then with nitrate of silver, changes with tolerable readiness, and darkens to a perfectly jet black. The photographs resulting from this process are very decided in their contrasts of black and white.

(220.) Sir John Herschel was the first who examined the combinations of the salts of lead and silver, and he found that the compound produced papers more sensitive than the silver alone. The use of lead was, however, abandoned, owing to the discoloration which went on in the dark, with greater or less rapidity, over the papers impregnated with its salts. Both gold and platinum interferes with the change set up by solar agency on the salts of silver; and where, even by using a large excess of the silver salt, a good photograph is procured, the gold or platinum continues to exert a decomposing power in the dark, which eventually destroys the picture. I am inclined to think the presence of copper with the silver is detrimental; a rather extensive series of experiments have shown that a small quantity of any of the soluble salts of this metal, rather quickens the change on the argentine salts at first. A certain portion of copper lessens the sensitiveness of the silver preparations, and has a tendency to destroy the paper. Iron has a decided property of accelerating the process of change; but it unfortunately continues the darkening influence when once set up, even when preserved in the dark. When we come to the con-

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sideration of the effects produced upon these metals and others, I shall have to point out some very striking properties of the salts of silver, which do not properly find a place here.

The descriptions of experiments on the less common salts of silver are retained, almost without alteration as in the first edition. It does not appear that these changes have been examined by any experimentalist, and I have had no opportunity of renewing this section of the inquiry. It is principally, therefore, with a view to establishing the date of the inquiry, that the latter paragraphs are preserved, with so little alteration.

(221.) It was expected that some important results would be obtained from the use of some of the fulminating compounds. The extreme danger attending the preparation of those remarkable combinations has been one cause, perhaps, why the experiments have been few and unsatisfactory. Some experiments which I made many years since, showed that those unstable compounds are capable of being employed as photographic agents of remarkable sensibility, provided they are used before any decomposition takes place. To give an example of the mode of proceeding adopted. Metallic silver was dissolved in nitric acid, and alcohol added to the solution with great caution, watching the moment when the mixture became cloudy, and, before any of the fulminate could be precipitated, checking the process by adding a sufficient quantity of water. Paper washed with this mixture changed to a very dark brown rapidly, and was found to be so sensitive that in a second or two in the camera obscura, pictures were obtained. In a few hours, however, the mixture was found to have lost its liability to change; it had, indeed, acquired so persistent a character, that, even in combination with the organic matter of the paper, and under the influence of the brightest sunshine, it resisted change for an hour or more, and eventually the mixture became absolutely unchangeable.

(222.) Alcohol and ether, simply combined with the solutions of silver, under some circumstances appear to render them more liable to change, but the advantages gained by the use of either, except for the colorific property which they possess, are not sufficiently great to induce their general application in photography. It is, however, quite certain, that some of the compounds belonging to the alcohol series possess very remarkable properties. Dr. Frankland has pointed out that the iodides and chlorides of ethyle do not act upon the metals in darkness, but that they combine in sunshine, or in diffused daylight\*, the quantity of gas liberated during the action being indeed an exact measure of the quantity of actinic force which has been exerted in a given time. This appears to indicate a plan by which we may measure with great exactness the relative proportions of light and actinism existing in the sunbeam at any given period.

(223.) Amongst the miscellaneous processes in photography which it becomes important to include in our investigations, is the FERROTYPE, as I ventured to name it some years since, in which the protosulphate of iron is employed as the developing agent instead of gallic acid, in many cases with the most evident advantage. The use of this salt is not confined to the iodide of silver, but, as I proved at the meeting of the British Association at York, it may be used as a developing agent upon nearly every salt of silver which has been employed as a photographic agent. The use of this salt was first indicated by me in 1844, and the value of it has never been disputed; the manner therefore in which it has been involved in certain photographic patents, though freely published to the world, is in the worst possible taste.

(224.) The Catalysotype, as a process introduced by Dr. Woods, of Parsonstown, was named; involving some peculiarities, requires especial notice. The process and its

\* Journal of the Chemical Society.



modifications are thus described by the inventor.\* “ While investigating the property which sugar possesses, in some instances, of preventing precipitation, I noticed that when syrup of ioduret of iron was mixed in certain proportions with solution of nitrate of silver, the precipitate was very quickly blackened when exposed to the light, and I thought that, if properly used, it might be employed with advantage as a photographic agent.

“ To enter very minutely into the particulars, or to explain the rationale of the process, would be too tedious; however, it is so simple, that those who will feel any pleasure in trying it will, I am sure, easily succeed, and to attempt any explanation of its theory would, in the present state of our knowledge, be advancing a mere hypothesis: I will, therefore, only state generally the method in which the paper is prepared, and then briefly giving my reasons for such parts of the process as are not at first sight obvious, will thereby enable the experimenter to be guarded against the failures that these precautions are intended to overcome.

“ Let well glazed paper be steeped in water to which hydrochloric acid has been added in the proportion of two drops to three ounces. When well wet, let it be washed over with a mixture of, syrup of ioduret of iron half a drachm, water two drachms and a half, tincture of iodine one drop.

“ When this has remained on the paper for a few minutes, so as to be imbibed, dry it lightly with bibulous paper, and being removed to a dark room, let it be washed over evenly, by means of a camel hair pencil, with a solution of nitrate of silver, ten grains to the ounce of distilled water. The paper is now ready for the camera, and the sooner it is used the better; as when the ingredients are not rightly mixed it is liable to spoil by keeping. The time I generally allow the paper to be exposed in the camera varies from two to thirty seconds; in clear weather, without sunshine, the medium is about fifteen seconds.

\* Journal of the Royal Irish Academy.

“ When the paper is removed from the camera no picture is visible. However, *when left in the dark, without any other preparation being used*, for a period which varies with the length of time it was exposed, and the strength of the light, a negative picture becomes gradually developed, until it arrives at a state of perfection which is not attained, I think, by photography produced by any other process. It would seem as if the salt of silver, being slightly affected by the light, though not in a degree to produce any visible effect on it if alone, sets up a catalytic action, which is extended to the salts of iron, and which continues after the stimulus of the light is withdrawn. The catalysis which then takes place has induced me to name this process, for want of a better word, the Catalysotype.

“ My reason for using the muriatic solution previous to washing with the ioduret of iron is this: I was for a long time tormented by seeing the pictures spoiled by yellow patches, and could not remedy it, until I observed that they presented an appearance as if that portion of the nitrate of silver which was not decomposed by the ioduret of iron had flowed away from the part. I then recollected that Sir J. Herschel and Mr. Robert Hunt had proved that iodide of silver is not very sensitive to light, unless some free nitrate be present. I accordingly tried to keep both together on the paper, and after many plans had failed, I succeeded by steeping it in the acid solution, which makes it freely and evenly imbibe whatever fluid is presented to it. I am sure that its utility is not confined to this effect, but it was for that purpose that I first employed it.

“ My reason for adding the tincture of iodine to the syrup is, that having in my first experiments made use of, with success, a syrup that had been for some time prepared, and afterwards remarking that fresh syrup did not answer so well, I examined both, and found in the former a little free iodine; I therefore added a little tincture of iodine with much benefit, and now always use it in quantities proportioned to the age of the syrup.

“If the syrup of the iodide of iron be used in too great quantity, the picture is dotted over with black spots, which afterwards change to white. If an excess of nitrate of silver be used, and a photograph immediately taken before the deposition of the oxide takes place, there will be often after some time a positive picture formed on the back of the negative one. The excess of the nitrate of silver makes the paper blacker where the light did not act on it, and this penetrates the paper; whereas the darkening produced by the light is confined to the surface. The maximum intensity of the spectrum on the paper, when a prism of crown glass is used, lies between the indigo and blue ray. The difference of effect of a strong and weak light is beautifully shown in the action of the spectrum: that part of the paper which is exposed to the indigo ray is coloured a reddish brown, and this is gradually darkened towards either extremity, until it becomes a deep black.

“While varying the process in endeavouring to find out the cause just mentioned, I discovered that the following proportions gave very fine negative pictures, from which good positive ones were obtained:—take of syrup of iodide of iron, distilled water, each two drachms; tincture of iodine, ten to twelve drops: mix. First brush this over the paper, and, after a few minutes, having dried it with the blotting paper, wash it over in the dark (before exposure in the camera) with the following solution, by means of a camel hair pencil:—take of nitrate of silver one drachm; pure water one ounce: mix. This gives a darker picture than the original preparation, and one better adapted for obtaining positive pictures.”

(225.) The employment of a film of albumen upon a glass plate, for the reception of the sensitive film, was introduced by M. Niepce de Saint Victor in 1848. Beyond the manipulation necessary to ensure a uniform coating on the glass plate of the white of eggs, there is little in this process which requires notice. The whites of fresh eggs are taken and beaten with a wooden fork into a white froth, and with this a solution of iodide of potassium is

combined; the mixture is then allowed to repose for a night, and the next day the viscous fluid, having deposited, is decanted off for use. This is spread uniformly over the glass plate, and, when hardened, dipped into a solution of nitrate of silver. Thus there is formed iodide of silver upon a surface of albumen. The pictures are obtained upon this surface by the use of gallic acid, and, in the hands of some operators, especially of Messrs. Ross and Thomson, of Edinburgh, it is susceptible of producing the most pictorial results.

(226.) The albumenized glass plate process is somewhat less sensitive than the more perfect processes on paper; the tenacious coating of albumen appearing to prevent the silver salt from changing so readily as it would otherwise do. I have chiefly introduced it here for the purpose of examining a very remarkable process devised by Mr. Fox Talbot, from the Catalysotype by Dr. Woods, already named, and my own process with the protosulphate of iron. There are, however, some peculiarities in the process which deserve more attention than they have yet received. The essential details of the process are as follows. A weak solution of nitrate of silver is mixed with alcohol; and pure albumen, being spread upon a glass plate, is washed with it. This gives great solidity and firmness to the albumen coat. A mixture is made of a solution of the prot-iodide of iron, alcohol, and acetic acid, and allowed to stand for a few days. During this a peculiar change takes place, and the mixture loses its acid smell, and acquires one which is peculiarly vinous. At this point it is in the most sensitive condition. The plate is washed with it, and then with a strong solution of nitrate of silver with acetic acid in combination. The plate is immediately placed in the camera obscura; it receives its impression; and this is developed by the use of the protosulphate of iron.\*

\* As many readers may desire to repeat this process, I have added Mr. Talbot's own description.

(227.) The peculiar action of the iodide of ethyle has been already named (222); and it appears to me, in the

“The mode of preparing the plates was as follows:—

“(1.) Take the most liquid portion of the white of an egg, rejecting the rest. Mix it with an equal quantity of water; spread it very evenly upon a plate of glass, and dry it at the fire: a strong heat may be used without injuring the plate. The film of dried albumen ought to be uniform and nearly invisible.

“(2.) To an aqueous solution of nitrate of silver add a considerable quantity of alcohol, so that an ounce of the mixture may contain three grains of the nitrate. I have tried various proportions, from one to six grains; but perhaps three grains answer best. More experiments are here required, since the results are much influenced by this part of the process.

“(3.) Dip the plate into this solution, and then let it dry spontaneously. Faint prismatic colours will then be seen upon the plate. It is important to remark, that the nitrate of silver appears to form a true chemical combination with the albumen, rendering it much harder and insoluble in liquids which dissolved it previously.

“(4.) Wash with distilled water, to remove any superfluous portions of the nitrate of silver; then give the plate a second coating of albumen similar to the first; but in drying it, avoid heating it too much, which would cause a commencement of decomposition of the silver. I have endeavoured to dispense with this operation No. 4., as it is not so easy to give a perfectly uniform coating of albumen as in No. 1.; but the inferiority of the results obtained without it induces me for the present to consider it necessary.

“(5.) To an aqueous solution of prot-iodide of iron add, first, an equal volume of acetic acid, and then ten volumes of alcohol. Allow the mixture to repose two or three days. At the end of that time it will have changed colour, and the odour of acetic acid, as well as that of alcohol, will have disappeared, and the liquid will have acquired a peculiar, but agreeable, vinous odour. It is in this state that I prefer to employ it.

“(6.) Into the iodide thus prepared and modified, the plate is dipped for a few seconds. All these operations may be performed by moderate daylight, avoiding, however, the direct solar rays.

“(7.) A solution is made of nitrate of silver, containing about seventy grains to one ounce of water. To three parts of this add two of acetic acid. Then, if the prepared plate is rapidly dipped once or twice into this solution, it acquires a very great degree of sensibility; and it ought then to be placed in the camera without delay.

“(8.) The plate is withdrawn from the camera, and, in order to bring out the image, it is dipped into a solution of protosulphate of iron, con-

process of change which goes on in the mixture of alcohol, acetic acid, and iodide of iron, when both the alcoholic and acid smells disappear and give place to a peculiar ethereal one, that some combination, analogous to the iodide of ethyle, is produced. The high sensibility of this process will be understood from an account of an experiment tried at the Royal Institution. A glass plate, prepared as I have described, was placed in a camera obscura properly adjusted in a dark room, so that it was in focus to receive the image of a revolving wheel. Upon the wheel was placed a printed bill; and when the wheel was making 200 revolutions in a second, it was illuminated by a spark from the discharge of a Leyden battery. Notwithstanding this rapid motion and transient illumination, the bill was faithfully printed on the photographic tablet.

(228.) Experiments are required to determine the changes which take place in this process, and to define

taining one part of the saturated solution diluted with two or three parts of water. The image appears very rapidly.

“(9.) Having washed the plate with water, it is now placed in a solution of hyposulphite of soda, which, in about a minute, causes the image to brighten up exceedingly by removing a kind of veil which previously covered it.

“(10.) The plate is then washed with distilled water; and the process is terminated. In order, however, to guard against future accidents, it is well to give the picture another coating of albumen or of varnish.

“These operations may appear long in the description, but they are rapidly enough executed after a little practice.

“In the process which I have now described, I trust that I have effected a harmonious combination of several previously-ascertained and valuable facts, especially of the photographic property of iodide, which was discovered by Dr. Woods of Parsonstown, in Ireland, and that of sulphate of iron, for which science is indebted to the researches of Mr. Robert Hunt. In the true adjustment of the proportions, and in the mode of operation, lies the difficulty of these investigations, since it is possible, by adopting other proportions and manipulations not very greatly differing from the above, and which a careless reader might consider to be the same, not only to fail in obtaining the highly-exalted sensibility which is desirable in this process, but actually to obtain scarcely any photographic result at all.”—*Athenæum*.

the causes upon which its high degree of sensibility depends. We know that modern chemists are disposed to regard alcohol as a peculiar hydrated oxide of ethyle. We also know that the ethyle has been combined with iodide, forming a kind of ether, and that this attacks, under the influences of the chemical rays or of heat, several of the metals. It is therefore important that the pure ethyle compounds, and others of an analogous character, should be tried as photographic agents. I have but little doubt that the remarkable sensibility of the collodion processes now to be described depends upon the action of some similar compound in combination with the salt of silver.

(229.) COLLODION PROCESS. — Collodion is gun-cotton dissolved in ether. Gun-cotton (pyroxylin) is prepared by acting upon cotton with nitric acid to which some sulphuric acid has been added; the object of the latter acid being the removal of water from the nitric acid. All gun-cottons are not soluble in ether; but, according to Vohl, they may be all rendered so by first boiling them in alcohol. The gun-cotton prepared by soaking in a saturated solution of nitrate of potash to which concentrated sulphuric acid has been added, is, after it has been well washed, soluble in ether, if some alcohol is present. Edwards informs us that a mixture of alcohol and ether of 0.76 to 0.77 sp. gr. dissolves gun-cotton instantly. We may prepare paper and many other substances in a similar manner to cotton; and when dissolved in ether, they all form a peculiar mucilaginous fluid — collodion — which is employed to form an artificial skin in cases of abraded wounds, and to coat glass with a delicate film for photographic purposes.

(230.) For photography the collodion is first iodized, as it is called. Iodide of potassium is dissolved in alcohol, and as much iodide of silver added as it will take up; and this is added to the collodion.

The iodized collodion is poured over a glass plate, which is moved about until a perfectly uniform film is formed. By the rapid evaporation of the ether, it speedily dries

and adheres with much firmness to the glass. The plate thus prepared is dipped into a solution of nitrate of silver by which it is covered with an iodide of silver, which is highly sensitive. It is now placed in the camera obscura to receive the radiant image, which, when the plate is properly prepared, it does in considerably less than a second of time. The image, as in the calotype process, is a dormant one; for the development of which a mixture of pyrogallic acid in distilled water, acetic acid, and nitrate of silver is poured over the plate. The impression becomes very intense, and is fixed in the usual manner with the hyposulphite of soda.

(231.) The negative collodion image can be converted into a positive one by several methods—all of them, however, depending upon the conversion of the film of darkened silver into a layer of brilliantly-white metallic silver. The best methods of doing this appears to be one of the following:—1st, protosulphate of iron, 20 grains; distilled water, 2 fluid ounces; nitric acid, 4 or 5 drops: or, 2nd, protonitrate of iron, obtained by decomposing nitrate of barytes, with the protosulphate of iron: or, 3rdly, by the use of a mixture of the protosulphate of iron and pyrogallic acid. Either of these solutions is poured over the plate; and in a short time a clear metallic image is obtained, which, when backed up with black velvet or a black varnish, is superior to the best effects of the daguerreotype.

(232.) It will from these statements be now sufficiently evident, that in those latter processes the alcohol and ether play a most important part. The collodion does not form merely a film upon which to spread the sensitive surface; it enters into direct combination with that sensitive agent, and the result is that exquisite sensibility for which the collodion process is remarkable.

(233.) The action of the prismatic spectrum upon a collodion plate is not a little remarkable. The impression is, of course, liable to some slight variations, dependent



upon the chemical constitution, and consequently, the sensibility of the preparation. The character of the bath from which the silver is constantly removed by the immersion of the iodized collodion on the glass, is constantly varying, and even the iodized collodion itself is liable to change, thus producing alterations in the sensitive surface, which, though inappreciable in the ordinary process of obtaining a picture, become well marked when we endeavour to impress it with an image of the prismatic spectrum.

(234.) The normal spectrum was formed by a very pure flint-glass prism. Light admitted between two knife-edges, separated  $\frac{1}{8}$ th of an inch, and generally passed through a hole of the same diameter in an inner screen. The chromatic image was received on a white tablet in a perfectly black box; its length, when most accurately adjusted, was 1 inch and  $\frac{3}{20}$ ths, which space has been divided into 100 parts; and to this division the numerical details refer. Chemical action commences .40 above the lower end of red, and from this point extends to the length of  $1\frac{1}{2}$  inch. Over the space covered by the red and orange rays are indications of a well-defined circle of protective action; immediately above this a dusky brown commences, forming a kind of fringing, which is extended to .60, and in a similar manner it bounds the whole of the spectrum. This is due to diffused light, which I always find bordering the spectrum. Over a space equal to .10 a well-defined black space appears; then the action weakens, but is still strong over .7, when it again increases just at the end of the violet, and is somewhat sharply cut off at 1.90 above 0, or lowest red, presenting an image similar to that represented in the margin. Placing the glass at a small angle, and observing the spectrum by reflexion, the lower dark space comes out very strongly, and the whole space



above it appears of a dark semi-metallic purple shaded by a dusky brown border. It is quite impossible to represent these delicate differences between the respective portions by a wood engraving. The accompanying figure is, therefore, to be regarded as representing with *accuracy* the general character of the impression, showing the limits of greatest and of least action, and little more.

(235.) By operating with a well-defined spectral image of a small slit, formed by the knife-edges, throwing this spectrum upon a large lens of long focus, and receiving the image at the distance of several feet from the lens on the collodion plate, we obtain a spectrum showing most of the dark lines of Fraunhofer, particularly those which are discovered at the most refrangible end of the spectrum, and over the space beyond the luminous rays, which is rendered luminous by the fluorescent rays of Professor Stokes, these being so many inactive spaces, which are in the first impression represented as so many white lines. A positive copy being taken from the negative spectrum, these are then represented correctly as dark lines, with an inversion of the character of the chemically darkened spaces. This, however, proves only that the modes of motion of Light and actinism are the same, it does not prove the identity of these forces. (*See frontispiece*).

## CHAPTER IV.

## SOLAR ACTION ON VARIOUS METALLIC COMPOUNDS.

(236.) GOLD.—It has been long known, that a solution of gold in ether decomposes by exposure to the sun's rays, metallic gold being deposited on the side of the vessel nearest the Light. Charcoal saturated with a solution of the chloride of gold, and exposed to the sun's rays, is speedily covered with a very fine film of the revived metal. Ivory may also be gilded by washing it with the same solution and exposure. Most of the salts of gold, indeed, are reduced by solar agency.

(237.) Sir John Herschel, in the *Philosophical Transactions*, Part I. for 1840, has given some very interesting particulars respecting some aurated preparations:—

Papers washed with CHLORIDE OF GOLD, freed from an excess of acid, are slowly changed under the influence of the solar beams, a regularly increasing darkness takes place, and the paper at length becomes purple (*Herschel*). I have observed that the first action of the Light is to whiten paper, which has been rendered a pale yellow by the wash of chloride of gold. If papers are removed from the Light when thus bleached, it will be found that a darkening action will gradually come on, and eventually develop the picture impressed on the paper. This process is much quickened by placing the paper in cold water, and, however slight the exposure may have been, the process of darkening continues until all the salt of gold is decomposed.

(238.) Chloride of gold with nitrate of silver gives a precipitate of a yellow brown colour, possibly metallic double salts, in which the gold as well as the silver is in the state of chloride. On glass this precipitate is but very

slightly sensitive; on paper it is blackened somewhat more speedily (*Herschel*).

(239.) If paper impregnated with oxalate of ammonia be washed with chloride of gold, it becomes, if certain proportions be hit, pretty sensitive to Light, passing rather rapidly to a violet purple in the sun (*Herschel*). I have found it exceedingly difficult to arrive at the best proportions: generally speaking, thirty grains of the oxalate of ammonia, and a saturated solution of the chloride of gold, has been the most successful in practice. These papers must be dried in the dark without heat. After the picture has been obtained, I have succeeded in fixing it, by soaking it in cold water, and then washing it over with the ferrocyanate of potash.

(240.) Paper impregnated with the acetate of lead, when washed with perfectly neutral chloride of gold, acquires a brownish-yellow hue, and a sensibility which, though not great, is attended with some peculiarities highly worthy of notice. The first impression of the sun's rays seems rather to whiten than to darken the paper, by discharging the original colour, and substituting for it a pale greyish tint, which by slow degrees increases to a dark slate colour; but if arrested, while yet not more than a moderate ash grey, and held in a current of *steam*, the colour of the part acted on by the solar rays (and of that only) darkens immediately to a deep purple: the same effect is produced by immersing it in boiling distilled water. If plunged into cold water, the same change comes on more slowly, and is not completed till the paper is dried by heat. A *dry heat*, however, does not operate this singular change (*Herschel*).

(241.) *Prismatic Analysis*. — Chloride of Gold. The maximum effect is produced by the mean blue ray, and the influence is exerted but a little way below the green; indeed, it is doubtful if it can be said, that any visible effect is produced below the green itself. Above the blue, the action is carried on, but with declining energy, through

the indigo and violet rays, beyond the most refrangible edge, of which no action can be detected.

To distinguish the following processes from the Chrysotype, which will be described in another section, I propose to designate them as *Aurotypes*.

(242.) *Aurotypes*. — Protocyanide of potassium and gold, prepared according to Himly's method\*, was washed over paper and dried; then it was washed with a solution of nitrate of silver, and again dried. This paper darkens with considerable rapidity, and this blackening proceeds steadily in the dark. Good photographs result from this preparation. The pictures are best fixed by soaking in a little salt and water, and then washing with a weak solution of the hyposulphite of soda.

(243.) It will be found that several of the combinations of the oxide of gold with cyanogen yield very interesting pictures, which promise to be of some importance in the photographic art. A few of these may be briefly mentioned.

(a) Protocyanide of potassium and gold, with a weak wash of nitrate of silver, changes with tolerable quickness, and presents a good contrast of light and shadow.

(b) Protocyanide of gold, formbenzoic acid, and nitrate of silver, give very beautiful results, and are tolerably quick in changing, although as yet no paper has been prepared, sufficiently sensitive for use in the camera obscura. The darkened portions are exceedingly intense, the impression being made nearly through the entire substance of the paper; hence affording very perfect photographs, from which copies of exceeding sharpness may be procured.

(c) Protocyanide of gold, formbenzoate of ammonia, and nitrate of silver, give results of an exceedingly pleasing kind. Papers thus prepared do not appear to be quite so sensitive as those which are prepared with the formo-

\* Appendix No. I.

benzoic acid, but they are sufficiently so for copying engravings in good sunshine.

(d) Nitrate of silver, protocyanide of potassium, and gold. A very delicate picture results from a short exposure to sunshine, which continues to darken without the aid of Light as long as any portion of gold remains undecomposed. It is a peculiar property of all the salts of gold, that the darkening process once set on foot is carried on in the dark as long as any gold remains.

(244.) *Prismatic Analysis.* — The following results, obtained upon several different preparations, will serve to exhibit most of the peculiarities which mark the influence of the solar beam or auriferous preparations.

On paper prepared as above (243. a). The maximum of action is far down in the blue rays, nearly on the verge of green. After a few minutes, the action is extended through the green ray to the very centre of the yellow ray. Towards the most refrangible end, the action is tolerably uniform through the whole of the blue and indigo rays; it slowly declines through the violet; but it extends with some considerable power over a space beyond the visible spectrum, equal to a third of its entire length.

A paper washed with the protocyanide of potassium and gold, between two washes of the nitrate of silver, exhibited the maximum of intensity on the very edge of the least refrangible blue ray. The darkening process was carried on, down to the edge of the orange ray; below which no action could be detected. Above the blue rays the influence became gradually weaker, and faded away entirely at a point beyond the violet rays, distant from the visible ray about the width of the violet rays themselves. No action could be detected at the least refrangible end of the spectrum.

A paper prepared as described (243. b) was acted upon with much energy. The maximum of action was in the mean blue ray; and a well-defined line marked the least refrangible edge of the rays. The influence was, however,

extended to the centre of the yellow ray, the action over the space occupied by the green rays being exceedingly well defined. At the most refrangible end the action was exerted with great energy up to the extreme edge of the visible violet rays; from which point it gradually declined, until the darkening entirely ceased at the extremity of a space beyond the violet, quite equal to half the length of the luminous spectrum. This paper had browned a little by keeping. This browning was entirely removed by the influence of the red rays, and to some extent bleached by all the rays along their lateral edges, presenting a similar phenomenon to that already described, as observed by Sir John Herschel on the tartrate of silver, and by myself on the Daguerreotype plates.

A paper prepared with a neutral solution of the chloride of gold, ammonia, and nitrate of silver, still exhibited the maximum effect in the blue ray; the darkening extending, however, with tolerable strength to the lower edge of the green rays, which impresses a decided green colour on the paper. The influence proceeds pretty equally through the blue and indigo rays; it diminishes through the violet, and ceases to act at the end of a space beyond the violet rays equal to three-eighths of the length of the visible spectrum.

A paper with protocyanide of gold, nitrate of silver, and ammonia, gave no evidence of any darkening action *within the luminous spectrum*. At the most refrangible edge of the violet rays, chemical action begins; and it rapidly reaches its maximum at a very short distance from it. A faint darkening goes on over a space equal to one half of the visible rays.

Papers prepared with the percyanide of potassium and gold, then formobenzoic acid and nitrate of silver, darken very rapidly over the whole extent of the most refrangible rays; the darkening commencing in the blue ray, and apparently going on through the whole period of exposure with greater energy about the mean ray of that colour

than in any other part. The influence is exerted with much power down to the red rays, and a second wash of the nitrate of silver carries the action below them. Over the violet end of the spectrum a very beautiful purple-brown colour is brought out, which fades into a lilac in the invisible rays, which exert their power with some energy over a considerable space.

(245.) If papers are carefully prepared with the percyanide of potassium and gold, &c., as the last named, they will be found exceedingly useful. If the preparations are pure, and the proportions in good adjustment, the results are most satisfactory, and the photographs are amongst the most beautiful that can be imagined. My own results do not enable me to fix with certainty the best proportions in which these agents should be united. It, however, appears that a saturated solution of the percyanide of potassium and gold, with formobenzoic acid, spec. grav. 1.12, and a solution of 100 grains of the nitrate of silver to an ounce of distilled water, are tolerably near the proportions required for the production of the most sensitive papers. I have, however, sometimes obtained very beautiful photographs with these agents united in different proportions from the above.

(246.) The action of oxalic acid on solutions of the salts of gold has been long known to chemists. When a neutral oxalate is heated with a neutral solution of gold, metallic gold is precipitated. Light acts the same part as heat. If a neutral chloride of gold and oxalate of potash be washed over paper and exposed to the sunshine, a slight change is immediately produced, which, however, goes on darkening until it assumes a very deep hue. Sir John Herschel remarks on this peculiarity, "A stain is produced, which, however feeble at first, under a certain dosage of the chloride, oxalate, and free acid, goes on increasing from day to day, and from week to week, when laid by in the dark, and especially in a damp atmosphere, till it acquires almost the blackness of ink, the unsunned



portion of the paper remaining unaffected, or so slightly as to render it almost certain that what little action of this kind exists is due to the effect of casual dispersed Light incident in the preparation of the paper. I have before me a specimen of paper so treated, in which the effect of thirty seconds' exposure to sunshine was quite invisible at first, and which is now of so intense a purple as may well be called a black, while the unsunned portion has acquired comparatively but a very slight brown. And (which is not a little remarkable, and indicates that in the time of exposure mentioned the *maximum* of effect was attained) other portions of the same paper exposed in graduated progression for longer times, viz. 1<sup>m</sup>, 2<sup>m</sup>, and 3<sup>m</sup>, are not in the least perceptible degree darker than the portion on which the light had acted during thirty seconds only."

(247.) Gold is not only thus affected when in combination with other salts; but any of the preparations of gold, having been exposed to the solar influence, go on "darkening spontaneously and very slowly, apparently without limit, so long as the least vestige of unreduced salt of gold remains in the paper." I find that on paper, after this decomposition of the chloride has been entirely effected, a change still goes on, and eventually a beautiful revival of gold gives a metallic appearance to the surface.

(248.) It has been stated, on the authority of Mr. Goddard, that a plate of gold is rendered very nearly as sensitive to luminous agency by the action of iodine vapour, as are the plates of silver used in the Daguerreotype process. I have not succeeded in rendering gold as sensitive as silver by either iodine or bromine; but it has been stated by Moser that all metallic plates are rendered to a certain degree photographically sensitive by being exposed to these vapours.

(249.) PLATINUM.—In 1832 Sir John Herschel communicated to the British Association at Oxford the curious fact, that when a solution of platinum in nitro-muriatic

acid has been neutralised by the addition of lime, and which has been well cleared by filtration, is mixed with lime-water in the dark, no precipitation to any considerable extent takes place—for a long while, indeed, none whatever; though after long standing, a slight flocky sediment is formed, after which the action is arrested entirely. But if the mixture, either freshly made, or when cleared by subsidence of this sediment, is exposed to sunshine, it instantly becomes milky, and a copious formation of a white precipitate (or a pale yellow one if the platinic solution be in excess) takes place, which subsides quickly, and is easily collected. The same takes place more slowly in cloudy daylight.

(250.) By exposing this mixture to Light which had permeated different coloured fluids, it was found that the action was confined entirely to the violet end of the spectrum. Sulphuric acid tincture of red-rose leaves protected the fluid entirely: an exposure of many days to full sunshine behind this fluid occasioned no precipitation, but it takes place instantly if exposed to full daylight, as copiously as if it had been all the time kept in total darkness. Yellow fluids, particularly a solution of the bichromate of potash, also serve to defend it.

(251.) When a solution of the chloride of platinum, as neutral as possible, is mixed with a saturated solution of the cyanide of potassium also boiling, a percyanide of potassium and platinum results. If paper is washed with this solution, and exposed to sunshine, a very faint change only is apparent, even after prolonged exposure. If, however, after a short time, the paper is taken into the dark, and washed with a solution of the protonitrate of mercury, a very pretty, though delicate positive picture results. The only mode by which any thing like permanence can be given to these pictures when formed, is by washing them in a dilute warm solution of carbonate of soda. Nearly all the PLATINOTYPES, however, slowly fade in the dark. This was written in 1844. I have,

however, now (1854) in my possession one of these pictures, which faded at first, but which gradually restored itself, until now, after ten years, it is quite perfect and permanent, transformed however from a negative to a positive picture.

(252.) On allowing the above solution to cool, a great number of minute crystals of a yellow colour are formed. By dissolving these in water a solution is made, which imparts to paper a much higher sensibility than the last-named preparation.

If either of these two papers, after they are taken from the sunshine, be washed over with a solution of the nitrate of silver, a positive picture is brought out, but it is, although perfect, exceedingly faint. If in this state, the paper is exposed to sunshine, it blackens over the portions which were uncovered, whilst the covered parts remain light, the result being a good negative picture.

(253.) If the solution of the percyanide of potassium and platinum is washed over paper, and after it is dried a solution of the protonitrate of mercury is applied, the paper becomes of a yellowish-brown tint. Exposed to sunshine, it gives a very peculiar picture, which will be either negative or positive, according to the depth of colour that comes on, which is exceedingly capricious. The exposed portions often pass into a beautiful vermilion colour, which, however, fades with some rapidity, leaving the ground of the paper a buff or ruddy brown.

(254.) *Prismatic Analysis.*—The action appears to commence at the same time, in the extreme yellow ray and in the blue. Commencing in the blue ray, the change of colour, or reddening, goes on through the violet ray; but it is confined, or very nearly so, to the visible spectrum. In the yellow ray a very positive blackening at first comes on; but this gradually passes away, and a bleaching action results. This bleaching is evident in copying of plants on this kind of paper, the parts covered

by the green leaves becoming pale as the other parts darken.

(255.) Percyanide of potassium and platinum, with one washing of nitrate of silver, affords a very pleasing result. The pictures procured on this kind of paper being of a well-defined deep lilac tint. A great many combinations of these two salts have been tried, and some of them give very pleasing photographs. If the nitrate of silver is in slight excess, and particularly if the silver is applied to the paper first, the impression is quite as strong on the wrong side of the paper as it is upon the right one. The iodide of potassium promises to be the most successful fixing agent for these kinds of platinotypes; but after a few months, although carefully preserved in a portfolio, little more than a blank sheet of white paper is left.

(256.) If, in addition to the nitrate of silver, we unite some corrosive sublimate, on the paper, with the platinum salt, an exposure of fifteen minutes produces but little apparent effect. If, however, on removing it from the Light, the paper is washed over with strong ammonia, a picture of intense blackness, on an iron-grey ground, is immediately produced. Heat brings the whole of the paper to one uniform iron-grey tinge. If the picture is placed in a solution of corrosive sublimate, a negative picture is very speedily produced by the dissolving out of the shadows.

(257.) CHLORIDE OF PLATINUM spread on paper undergoes some change very speedily, although this is not often evident until it is afterwards washed over with the proto-nitrate of mercury. A great variety of combinations have been made the subjects of experiment. The chloride of platinum has been united with oxalic acid, tartaric acid, formic acid, and a great many of these compounds in which cyanogen plays an important part. The results have been pretty much the same in all: in some cases the action of the solar rays is to deepen the yellow colour

of the paper, in others, to bleach it; and hence when the subsequent washing with the mercurial solution is given, sometimes a positive and sometimes a negative image results. All the combinations with the ferroproussiates have exhibited, by a decomposition of these salts, very pleasing blue grounds.

(258.) IODIDE OF PLATINUM. — Sir John Herschel was the first to call attention to the sensibility of paper prepared with the iodide of platinum. In a few minutes a very decided image is formed upon it; but this rapidly fades out, the sensibility of the paper not being at all impaired, even after repeated exposures to Light.

(259.) BROMIDE OF PLATINUM exhibits the same peculiarities as the iodide. I have tried upon these preparations a great many fixing agents, without being quite successful with any. It appears, indeed, to be a distinguishing characteristic of the salts of this metal, that, in the dark, they have the power of overcoming the change which has been produced by the solar rays, and of restoring themselves to their original state. The kind of change brought about by exposure is not very evident: in some cases the yellow platinum salts are darkened, in others bleached; in either case, if these papers are put aside, the original yellow is restored.

(260.) In Sir John Herschel's Memoir on the Chemical Action of the Rays of the Solar Spectrum, some peculiar phenomena exhibited by the chloride and iodide of this metal are named, which it is important I should transfer to my pages, corroborating in a striking manner the capricious nature, under the influence of the solar rays, of the salts of this singular metal:—

“A solution of chloride of platinum in ether being washed over a bibulous paper impregnated with hydriodate of potash, in certain degrees of strength and copiousness, browns pretty rapidly in the dark, but much more rapidly, and to a much deeper tint, in sunshine. A paper so washed and partly shaded, on exposure, pro-

duced a well-defined figure of the shading body, which, on the addition of a fresh wash of the hydriodate, *out of the Light*, became much more strongly contrasted with the surrounding ground."

(261.) "Paper washed with acetate of lead, and then with chloride of platina, is absolutely insensible, and only becomes very freely so when thoroughly impregnated with nitrate of silver. But if in place of the nitrate of silver, a wash of hydriodate of potash be superadded, the effect is remarkable. If the hydriodic solution be strong and plentiful, the paper is immediately coloured dark brown, whether in Light or darkness. If very weak, no effect; but if applied of a certain intermediate strength, though not *immediately* affected in the shade, yet, if held (while wet) in the sun, it darkens with extraordinary rapidity to the same deep brown hue, *and presently after, the exposure to the sun continuing whitens again*. A fresh dose of the hydriodate being applied, it again darkens, but is no longer capable of restoration, and the darkness goes on increasing to a fine deep chocolate brown."

(262.) From the powerful influence exerted by the oxalate of the protoxide of iron on the salts of platinum, I was led to hope that this combination might be brought under the agency of the sun's rays, to such an extent as to render it available as a photographic agent; but the action is not so much accelerated by the sun as to render its issue of any value. If a paper prepared with a tolerably strong solution of the oxalate, and a solution of the chloride of platinum, made neutral by carbonate of soda, is exposed, with one portion carefully screened, for only a few minutes, it will be found that the uncovered portion is by far the darkest, and for a certain period this darkening goes on, even out of the Light; but after a time a bleaching action commences, and, unless an additional quantity of the oxalate is applied, all evidence of solar influence is erased.

(263.) Having placed a number of photographs pre-

pared with salts of platinum in a portfolio with others which had been taken on papers spread with silver salts, I was somewhat surprised to find that, although the pictures on the platinum papers were faded out, very good images of these pictures, dark upon a light ground, were left upon the argentine papers. This curious action would appear to point to a method by which these evanescent pictures may be made to leave very good positive images behind, by being placed in juxtaposition with other photographic papers.

(264.) MERCURY. — It has long been known to chemists that the protoxide of mercury is very liable to resolve itself into the peroxide and metallic mercury, under the influence of the direct solar rays, or even of daylight. The peroxide also, it has been stated by Guibourt, is converted into metallic mercury and oxygen by long exposure. This, I find, may be effected with some degree of rapidity, and the peroxide used for the production of really interesting photographic drawings. If red precipitate is ground to a very fine powder, and well incorporated with gum water, it may be applied upon paper very evenly with a camel's hair brush, and it dries, forming a fine red surface. If paper thus prepared is exposed, with an engraving upon it, to good sunshine, for ten or twelve hours, all the exposed parts are deeply blackened, and those under the white parts of the engraving changed to a deep olive, thus giving a negative photograph, which is somewhat singular in its appearance and colours, which are red, olive, and black. If these papers are, after having been thus darkened, washed with water, the peroxide of mercury is removed, and a faint brown stain only, left upon the paper, over the parts which were covered with the darkened oxide. I have observed that the peroxide of mercury kept in a bottle, near a window into which the sun shines during the greater portion of the day, slowly changes to a deep yellow colour, and is, on the side next the Light, reduced

to a fine powder, which adheres with tolerable firmness to the glass.

(265.) CARBONATE OF MERCURY, it is well known, parts with carbonic acid in contact with the air, and becomes brown, even in the dark. If, when recently prepared, it is exposed to Light, a very rapid darkening is brought on, which, it appears probable, may be advantageously employed in varying our photographic specimens. The best mode of preparing this kind of mercurial paper with which I am acquainted, is to wash good writing paper with a saturated solution of the protonitrate of mercury. It must then be dried as quickly as possible, without bringing it too near the fire, which very rapidly, if hot, decomposes the salt, when in contact with organic matter. A moderately strong solution of the carbonate of potash is then applied. If exposed whilst wet, provided there is good sunshine, this preparation darkens to a good black in a few minutes. If carefully dried between folds of blotting paper, and exposed in a dry state, the darkening is still more rapid.

(266.) *Prismatic Analysis*.—The action of the spectrum appears to be limited to a space, between the lower edge of the blue and the extreme limits of the violet rays, over which the darkening is very rapid; the other rays appear to be nearly without action, although by carefully heating the paper after exposure up to the point at which decomposition is effected, it becomes evident that some influence has been exerted beyond the visible violet, and also about the region of the yellow rays, as these parts are the first which exhibit any symptoms of change by calorific agency.

(267.) "Protonitrate of mercury, simply washed over paper, is slowly and feebly blackened by exposure to sunshine." This was first observed by Sir John Herschel, who, by taking advantage of the properties of some of the protosalts of iron, produced some very curious photographic results, which must now be described. If paper is



impregnated with the ammonia-citrate of iron, and one portion of it being covered, the other part is exposed to the sun, and then washed with the protonitrate, this salt is slowly reduced over the sunned portion.

(268.) If the protonitrate of mercury is mixed with either the ammonia-citrate or citrate of iron, a precipitate is produced. Sir John Herschel recommends one measure of a solution of ammonia-citrate, and one of a solution of ammonia-tartrate of iron, containing, each, one tenth of its weight of the respective salts; tartaric acid, a saturated solution, one eighth of the joint volumes of the other solutions. Form a cream, by pouring in rapidly, one measure of a saturated solution of the protonitrate, and well mixing with a brush. This cream should be spread very quickly over the whole paper, well worked in, cleared off as much as possible, and finished with a brush nearly dry, spread out broad, and pressed to a straight thin edge, which must be drawn as lightly and evenly as possible over every part of the paper, until the surface appears free from every streak, and barely moist. "About half an hour, or an hour, according to the sun, affords pictures of such force and depth of colour, such velvety richness of material, and such perfection of detail and preservation of the relative intensities of the Light, as infinitely to surpass any photographic production I have yet seen, and which indeed it seems impossible to go beyond. Most unfortunately they cannot be preserved. Every attempt to fix them has resulted in the destruction of their beauty and force; and even when kept from Light, they fade with more or less rapidity, some disappearing almost entirely in three or four days, while others have resisted tolerably well for a fortnight, or even a month. It is to an overdose of the tartaric acid that their more rapid deterioration seems to be due; and of course it is important to keep down the proportion of this ingredient as low as possible; but without it I have never succeeded in producing that peculiar velvety aspect, on which the charm of these pictures chiefly depends, nor

anything like the same intensity of colour without over-sunning."

(269.) Another very interesting combination is the following:—"Let a paper be washed over with a weak solution of periodide of iron, and, when dry, with a solution of protonitrate of mercury. A bright yellow paper is produced, which (if the right strength of the liquids be hit) is exceedingly sensitive while wet, darkening to a brown colour in a very few seconds in the sunshine. Withdrawn, the impression fades rapidly, and the paper in a few hours recovers its original colour. In operating this change of colour the whole spectrum is effective, with the exception of the thermic rays beyond the red." (*Herschel.*)

(270.) DEUTIODIDE OF MERCURY—formed with a persalt of mercury and the iodide of potassium. During good sunshine this preparation darkens very distinctly in fifteen minutes: an hour's exposure brought on a full brown colour. If, after exposure to the sun, paper on which it may have been spread is gently warmed by the fire, the brown colour fades quite away, leaving the paper of a bright red.

(271.) I have combined the protonitrate of mercury with a great number of the organic acids and their salts. Some change is very evident upon all that have yet been tried, the sun, in spaces of time varying from five minutes to as many hours, producing very marked evidences of its decomposing power. The formiates, benzoates, and galates, are the most decided in their action; and if, after a short exposure, papers prepared with these salts are washed over with the oxalate of iron, tolerably good pictures are produced.

(272.) The pernitrates of mercury and the yellow subsalt which is formed when the nitrate is put into hot water, have both been made the subjects of experiment. They have, when used alone on paper, and when united with other metallic and alkaline salts, given decided evidence of change under the sun's rays, but not to such an extent

as appears to warrant any hope of their being of much photographic value.

(273.) Subnitrate of mercury and the benzoate of the hydruret of benzole, were united on paper, and in half an hour of good sunshine a very fair picture was formed, the darkened parts being of a deep buff colour. The picture rapidly faded out, but it could at any time be restored by washing it over with the hyposulphite of soda, or the protosulphate of iron.

(274.) NITRATE OF MERCURY and ferroproussiatic of potash.—Even in the dark the latter salt is slowly decomposed by the mercurial compound, and the paper discoloured by the formation of prussian blue. In the sunshine this is very rapidly produced, after which a bleaching action comes on. If after the bleaching process has been carried on until the paper is nearly white, it is removed from the Light, and washed over with a saturated solution of nitrate of silver, a positive image is produced. The protonitrate of mercury and the red prussiate of potash undergo nearly the same changes as the above.

(275.) CHROMATE OF MERCURY, formed from a solution of the nitrate of mercury and the bichromate of potash, is rapidly darkened under the first impulse of the solar action; it then bleaches, but somewhat more slowly. If papers thus prepared are now removed from the Light, and washed over with a solution of nitrate of silver, very beautiful pictures of a fine red colour are produced: these are rendered permanent by washing with a very weak solution of a mercurial salt; at least, as it regards Light. They still change under the influence of time, and some of the transformations which they undergo are exceedingly curious. They usually fade out entirely over the side of the paper which has been exposed, and on which the picture was at first formed; but as the picture vanishes from the front of the paper, it slowly develops itself on the back, not of the same red colour, but the metal is revived, and we have a semi-metallic picture of much interest. Could we depend

upon the change taking place in a regular manner, we should have the means of producing very beautiful and curious photographs. (See *Chromate of Copper—Chromatypes.*)

(276.) Many other mercurial salts spread upon paper, and precipitated upon glass, have been experimented with; and although no results sufficiently certain to warrant the publication of them have been obtained, yet most decided evidences have been afforded that all these salts are liable to decomposition under the influence of the solar rays. On many of them the invisible radiations from hot iron have a very powerful effect; and these are not, as might have been expected, much influenced by the calorific rays of the spectrum. This seems to point to some difference between the solar and terrestrial radiations. From time to time I have returned to my experiments with the mercurial salts, but they have been so interrupted, that at the present date (1854) I am unable to add anything new to the above researches, made in 1844.

(277.) IRON.—For nearly the whole of the facts connected with the photographic properties of the salts of iron we are indebted to the labours of Sir John Herschel. In his hands these salts have become valuable photographic agents; and two or three processes which have been devised, are among the most interesting within the range of the photographic art, whether we regard the beauties of the pictures which are formed, or the singular changes which take place upon them. I have repeated all Sir John Herschel's published experiments with much care, but I have little to add to what he had already observed and published. I shall therefore extract largely from Sir John Herschel's Memoir, and merely add such remarks of my own as may appear to explain any of the processes more fully.

(278.) THE CHRYSOTYPE.—“Paper is washed with a moderately concentrated solution of ammonia-citrate of iron, and dried; the strength of the solution being such as

to dry into a good yellow colour, and not at all brown. In this state it is ready to receive a photographic image, which may be impressed on it, either from nature in the camera obscura, or from an engraving on a frame in sunshine. The image so impressed, however, is faint, and sometimes hardly perceptible. The moment it is removed from the frame or camera, it must be washed over with a neutral solution of gold, of such strength as to have the colour of sherry wine. Instantly the picture appears, not indeed at once of its full intensity, but darkening with great rapidity up to a certain point, depending on the strength of the solutions used, &c. At this point nothing can surpass the sharpness and perfection of detail of the resulting photograph. To arrest this process, and to fix the picture (so far at least as the agency of *Light* is concerned), it is to be thrown into water slightly acidulated with sulphuric acid and well soaked, dried, washed with bromide of potassium, rinsed, and dried again."

(279.) Subsequently the discoverer of this process recommended the iodide of potassium as superior to the bromide as a fixing agent. "As soon as the picture is satisfactorily brought out by the auriferous fluid, it is to be rinsed in spring water, which must be three times renewed. It is then blotted off and dried, after which it is to be washed on both sides with a somewhat weak solution iodide of potassium. If there be any free chloride of gold present in the pores of the paper it will be discoloured, the lights passing to a ruddy brown; but they speedily whiten again spontaneously, or at all events on throwing it (after lying a minute or two) into fresh water, in which being again rinsed and dried, it is now perfectly fixed."

(280.) If instead of a solution of gold the nitrate of silver is used, the picture is brought out somewhat more slowly, and, as far as my own experience goes, with much less beauty, whether we consider colour or detail.

(281.) CYANOTYPE.—This name has been applied by Sir John Herschel to the whole class of processes in which

cyanogen in its combinations with iron form a leading principle. The following constitute the most interesting of this class.

1. A paper is prepared as above with the ammonia citrate of iron, and a latent picture is impressed upon it. If the action of Light has been carried on to the darkening of the paper, the picture is negative. Over this picture a solution of the ferroproussiate of potash, in which is dissolved a little gum arabic, is very sparingly but equally applied. As soon as this is done, the negative image vanishes, and by slow degrees is replaced by a positive one of a violet blue colour on a greenish yellow ground. If when *dry* the picture is not so distinct as could be desired, a second wash is applied; and when the image is fully developed, which it is with exceeding beauty if the operation has been carefully performed, the paper must be dried as speedily as possible. No fixing is required; the picture becomes pale in a very strong light, but it recovers its original colour in the dark.

2. Mix together ammonia citrate of iron and sulphocyanate of potash in solution, and to the mixture add a small quantity of nitric acid. If only a certain portion of acid be added, the resulting red liquid spread on paper, whitens spontaneously. This is not the case if more acid is added; but paper washed with the superacidulated solution, retains when dry a considerable degree of colour, and receives a positive image with great rapidity, which appears more distinctly at the back of the paper than on its face. These impressions have not yet been successfully fixed.

3. With a mixture which may contain equal proportions of ammonia-citrate of iron and ferrosesquicyanate of potash prepare a paper, and impress it with a picture, after which throw it into water and dry it; a *negative blue* picture will be produced. If this picture is washed with a solution of the protonitrate of mercury, it is in little time discharged. The mercurial salt being thoroughly

washed out, and the paper dried, the picture is susceptible of restoration. If a smooth iron is passed over it somewhat hotter than is used for ironing linen, but not sufficiently so as to scorch the paper, the obliterated picture immediately reappears, not blue, *but brown*. However carefully kept, these photographs fade after a few weeks and disappear. A fresh application of heat restores them to full intensity.

4. This use of a mercurial salt led Sir John Herschel to devise an improvement on the cyanotype process, No. 1., which affords much more certain results and more decided pictures. One part by weight of the ammonia-citrate of iron is dissolved in eleven parts of water, and this is mixed with an equal quantity of a saturated cold solution of corrosive sublimate (bichloride of mercury). Before a precipitate has had time to form the solution is washed over paper (which should have rather a yellowish than a bluish cast) and dried. This paper appears to keep well. It is exposed to Light till a faint, but perfectly visible picture is impressed. It is then washed over as rapidly as possible with a broad flat brush, dipped in a saturated solution of prussiate of potash, diluted with three times its bulk of gum water, so strong as just to flow freely without adhesion to the lip of the vessel. Care is required to spread this wash with one application, evenly, over every part of the paper. Beautiful pictures are thus produced, which will immediately bear exposure to Light tolerably well, but which after a few days will bear strong sunshine uninjured. By long keeping, details which were barely seen at first, come out with continually increasing intensity.

5. Wash a paper with a solution of the ammonia-citrate of iron and dry it; then wash it over with a solution of the ferrocyanate of potash; there is no immediate formation of true prussian blue, but the paper rapidly acquires a deep purple colour. If in this state these papers are exposed to Light, they give positive pictures of

great sharpness; but they possess this peculiarity—they darken again spontaneously on exposure to the air in darkness, and are soon obliterated. The paper, however, remains susceptible to Light, and capable of receiving other pictures, which fade in their turn. If these pictures are washed with ammonia or its carbonate, they are for a few moments obliterated, but they presently reappear, with *reversed lights and shades*. “In this state they are fixed, and the ammonia, with all that it will dissolve, being removed by washing in water, their colour becomes a pure prussian blue, which deepens much by keeping. If the solutions be mixed, there results a very dark violet-coloured ink, which may be kept uninjured in an opaque bottle, and will readily furnish by a single wash, at a moment’s notice, the positive paper in question, which is most sensitive when wet.”

6. Paper simply washed with the ferrosesquicyanuret of potassium, is highly sensitive to Light. Exposed to sunshine for about an hour, with an engraving upon it, a beautiful negative photograph is the result. These are fixed by soaking in water in which a little sulphate of soda is dissolved, to ensure the fixity of the prussian blue deposited. While dry this cyanotype is dove-colour on a greenish yellow ground; after washing, it becomes bright blue on a white ground.

7. Prepare a paper by washing, first, with a weak solution of ammonia-citrate of iron, one part by weight of the salt to twenty parts of water, and, when dry, with a saturated solution of the protonitrate of mercury. When nearly dry expose it for twenty minutes or half an hour to the Light, and a faint photograph will result. If it is now wetted with water and held for a few minutes in the sun, every part of the picture becomes visible, each line assuming an inky blackness. Instead of water, the solution of the nitrate of mercury may be used, and it possesses the advantage of giving greater permanence to the picture than when it was excited by water only.



(282.) The rationale of these processes has been well explained by their talented discoverer. In nearly all cases the action of the sun's rays is a deoxidising one. In the case of the ferrosesquicyanuret of potassium, No. 6., oxygen is parted with, which combines with hydrogen to form water. Prussian blue is deposited, the base being supplied by the destruction of one portion of the ferrocyanic acid, and the acid by the destruction of another. The change which takes place in the other cyanotype processes is somewhat more complicated.

“ It seems at first sight natural to refer these curious and complex changes to the instability of the cyanic compounds; and that this opinion is to a certain extent correct is proved by the photographic impressions received on papers, which have no iron but what exists in the ferrocyanic salts themselves. Nevertheless, the following experiments abundantly prove that in several of the changes above described, the *immediate action* of the solar rays is not exerted on these salts, but on the iron contained in the ferruginous solutions, added to them, which it deoxidises or otherwise alters, thereby presenting it to the ferrocyanic salts in such a form as to precipitate the acids in combination with the peroxide or protoxide of iron, as the case may be. To make this evident, all that is necessary is simply to *leave out the ferrocyanate* in the preparation of the paper, which thus becomes reduced to a simple washing over with the ammoniacitric solution. \* \* \* If a slip of this paper be held for only four or five seconds in the sun (the effect of which is quite imperceptible to the eye), and when withdrawn into the shade be washed over with the ferrosesquicyanate of potash, a considerable deposit of prussian blue takes place on the sunned part, and none whatever on the rest, so that on washing the whole with water, a pretty strong blue impression is left, demonstrating the reduction of iron in that portion of the paper to the state of protoxide. The effect in question is not, it should be observed, peculiar to the ammoniacitrate of iron.

The ammonia- and potassio-tartrate fully possess, and the perchloride, *exactly neutralised*, partakes of the same property: but the experiment is far more neatly made, and succeeds better, with the other salts." (*Herschel*).

I have found that nearly all the salts of iron, under the influence of the sun's rays, for a longer or shorter period, undergo the same kind of decomposition, and to a certain extent, exhibit the same phenomena when washed with the ferrocyanates.

(283.) *Prismatic Analysis.* — (*Herschel*.) Papers washed with the ferrosesquicyanuret of potassium exposed to the prismatic spectrum, prove that the decomposition of the salt, and deposit of prussian blue, is due to the action of the blue and violet rays below the blue, having absolutely no influence. The greatest activity appears to exist about the region of the indigo rays.

(284.) If this salt is mixed with perchloride of iron, and washed over paper, whilst it is exposed to the spectrum, the action is continued down to the very end of the thermic spectrum. The formation of the deposit colour in this region is accompanied with phenomena of a novel character, referable to the heat developed by the thermic spectrum. Oval brown spots are formed, which correspond with the heat spots referred to, and which are evidently due to calorific agency. If ammonia-citrate of iron is used instead of the perchloride, "a copious and richly-coloured deposit of Prussian blue is formed over the whole of the blue, violet, and extra spectral rays in that direction, extending downward (with rapid graduation) almost to the yellow." If the action of Light is continued, the blue and violet rays in a very strange way destroy their own work: "a *white* oval makes its appearance in the most intense part of the blue, which extends rapidly upwards and downwards. At a certain point of the action, the upper or more refrangible extremity of the white impression exhibits a semicircular termination, beyond which is a distinct and tolerably well-defined *conjugate image*, or

insulated circular white spot, whose centre is situated far beyond the extreme visible violet."

(285.) Sir John Herschel also examined the action of the prismatic rays on the ordinary ferrocyanuret of potash, which it is well known undergoes a change slowly in the sunshine, depositing Prussian blue. Paper washed with a fresh solution of this salt, slowly deposits when exposed to the spectrum, Prussian blue over the region of the blue, violet, and lavender rays, whilst the formation of a violet-coloured streak takes place, where the violet ray is most intense. The action of the calorific rays is very strongly marked, when the decomposition of the salt is assisted by a wash of dilute sulphuric acid. The impression is at first greenish, but as it blends with the upper portions of the spectrum, it passes into blue; the ground upon which this *streak* is impressed being a brown, which appears to form, as it were, a narrow border around it.

(286.) We are indebted to Sir John Herschel also, for a very remarkable process, in which the dormant pictures are developed by the breath or a damp atmosphere. This process was announced at the Cork Meeting of the British Association in August, 1843, and was published immediately in the *Athenæum* of September the 16th, from which publication the particulars of the process are extracted.

If nitrate of silver, specific gravity 1·200, be added to ferro-tartaric acid, specific gravity 1·023, a precipitate falls, which is in a great measure re-dissolved by a gentle heat, leaving a black sediment, which being cleared by subsidence, a liquid of a pale yellow colour is obtained, in which a further addition of the nitrate causes no turbidness. When the total quantity of the nitrated solution added amounts to about half the bulk of the ferro-tartaric acid, it is enough. The liquid so prepared does not alter by keeping in the dark. Spread on paper and exposed *wet* to sunshine (partly shaded) for a few seconds, no impression seems to have been made, but by degrees, although

withdrawn from the Light, it develops itself spontaneously, and at length becomes very intense. But if the paper be thoroughly dried in the dark (in which state it is of a very pale greenish yellow colour), it possesses the singular property, of receiving a dormant or invisible picture, to produce which (if it be, for instance, an engraving that is to be copied), from thirty seconds to a minute's exposure in the sunshine is requisite. It should not be continued too long, as not only is the ultimate effect less striking, but a picture begins to be *visibly* produced, which darkens spontaneously after it is withdrawn. But if the exposure be discontinued before this effect comes on, an invisible impression is the result, to develop which, all that is necessary is to breathe upon it, when it immediately appears, and very speedily acquires an extraordinary intensity and sharpness, as if by magic. Instead of the breath, it may be subjected to the regulated action of aqueous vapour, by laying it in a blotting-paper book, of which some of the outer leaves on both sides have been damped, or by holding it over warm water. Many preparations of gold and silver possess a similar property in an inferior degree.

(287.) *The AMPHITYPE.* In 1844, at the York Meeting of the British Association, Sir J. Herschel communicated the following:—Paper proper for producing an amphitype picture may be prepared either with the ferro-tartrate or ferro-citrate of the protoxide or the peroxide of mercury, or of the protoxide of lead, by using creams of these salts, or by successive applications of the nitrates of the respective oxides, singly or in mixture, to the paper, alternating with solutions of the ammonia tartrate or ammonia of citrate of iron, the latter solutions being last applied, and in more or less excess. I purposely avoid stating proportions, as I have not yet been able to fix upon any which certainly succeed. Paper so prepared and dried takes a negative picture, in a time varying from half an hour to five or six hours, according to the

intensity of the light; and the impression produced varies in apparent force from a faint and hardly perceptible picture to one of the highest conceivable fullness and richness both of line and detail, the colour in this case being of a superb velvety brown. This extreme richness of effect is not produced except lead be present, either in the ingredients used or *in the paper itself*. It is not, as I originally supposed, due to the presence of free tartaric acid. The pictures in this state are not permanent. They fade in the dark, though with very different degrees of rapidity, some (especially if free tartaric or citric acid be present) in a few days, while others remain for weeks unimpaired, and require whole years for their total obliteration. But though entirely faded out in appearance, the picture is only rendered dormant, and may be restored, changing its character from negative to positive, and its colour from brown to black (in the shadow) by the following process : — A bath being prepared by procuring a small quantity of solution of pernitrate of mercury into a large quantity of water, and letting the sub-nitrated precipitate subside, the picture must be immersed in it (carefully and repeatedly clearing off all air bubbles), and allowed to remain till the picture (if anywhere visible) is entirely destroyed, or if faded, till it is judged sufficient from previous experience; a term which is often marked by the appearance of a feeble positive picture, of a bright yellow hue, on the pale yellow ground of the paper. A long time (several weeks) is often required for this, but heat accelerates the action, and it is often complete in a few hours. In this state the picture is to be very thoroughly rinsed and soaked in pure warm water and then dried. It is then to be well ironed with a smooth iron, heated so as barely not to injure the paper, placing it, for better security against scorching, between clean smooth papers. If then the process have been successful, a perfectly black, positive picture is developed. At first it most commonly happens that the whole picture is sooty

or dingy to such a degree that it is condemned as spoiled ; but on keeping it between the leaves of a book, especially in a moist atmosphere, by extremely slow degrees this dinginess disappears, and the picture disengages itself with continually increasing sharpness and clearness, and acquires the exact effect of a copper-plate engraving on a paper more or less tinted with pale yellow. I ought to observe, that the best and most uniform specimens which I have procured have been on paper previously washed with certain preparations of uric acid, which is a very remarkable and powerful photographic element. The intensity of the original negative picture is no criterion of what may be expressed in the positive. It is from the production, by one and the same action of the Light, of either a positive or a negative picture, according to the subsequent manipulations, that I have designated the process thus generally sketched out by the term *amphitype*, — a name suggested by Mr. Talbot, to whom I communicated this singular result ; and to this process or class of processes (which I cannot doubt when pursued will lead to some very beautiful results) I propose to restrict the name in question.

(288.) It may not be uninteresting to add a few brief remarks on some of the salts of iron, to which Sir John Herschel did not extend his observations, or at least which have not been recommended by him as photographic agents. OXALATE OF IRON in solution, to which an excess of oxalic acid has been added, affords after a few minutes' exposure, when washed with nitrate of silver, a very intense black picture, which slowly fades into a dingy grey. If the oxalate of iron and silver be combined in the paper, and exposed, so powerful a picture results, that it is difficult to tell the right from the wrong side, the impression penetrating quite through the paper.

(289.) Oxalate of iron, with an excess of acid, washed over paper, and then a wash of ferrocyanide of potassium, gives a very faint blue paper, which blue colour is entirely

discharged if the acid is in large excess; if, however, the proportions are so adjusted that a little blue is still left on the paper, it is exceedingly sensitive to the sun's rays, the colour being very rapidly discharged. If after exposure, the paper is washed over with nitrate of silver, chloride of mercury, or a neutral solution of gold, a blue picture of much intensity results, which may be rendered tolerably permanent either by a wash of the ferrocyanide itself, or by a solution of the iodide of potassium.

(290.) IODIDE OF IRON loses colour in the sunshine, and on paper, gives a positive picture; the subsequent application of the nitrate of silver has not been, with me, in any way successful in improving the faint picture it gives.

(291.) CHROMATE OF IRON changes but very slightly in colour by exposure; but if spread on glass or paper, and exposed, one part being shaded, and afterwards it is washed over with the nitrate of silver, the chromate of silver is formed over one portion, but not over the other. It is necessary that the chromate of iron should be newly formed.

(292.) As far as my researches have gone, all the persalts of iron are converted into protosalts by exposure to sunshine, when in combination with organic matter. This has been most fully confirmed, and even in soils all the persalts are changed to protosalts of iron by the action of growing vegetable and Light. I have reasons for believing that all the protosalts undergo some change, it being very evident that exposed and unexposed portions of papers washed with solutions of the protosalts act very differently upon solutions of gold and silver. What this change may be it is impossible to say in the present stage of our inquiry, but it will be seen that scarcely any of the metallic salts resist the agency of the sun's rays.

(293.) COPPER.—It had been long known to me that plates of copper could be rendered sensitive to solar influence, by being submitted to iodine vapour. In a very early stage of my experiments with the Daguerreotype—

indeed, before the publication of the process pursued by Daguerre—in conjunction with Mr. Towson—I operated with pure copper plates; and some results obtained at that time were of considerable promise. The publication of any account of a process, by which photographs might be taken upon copper, was first made by Mr. Fox Talbot, who has included it in his extensive list of Patents under the title of “improvements in obtaining pictures or representations of objects by the action of Light.” The process is as follows:—A polished copper plate is exposed to the vapour of iodine or bromine, or the two substances combined, or either of them in combination with chlorine. Or the copper plate may be immersed in a solution made by dissolving one of the above-mentioned substances in alcohol or some other solvent. The plate is now placed in the camera, and after it has remained in it for a period varying, according to my own experiments, from twenty minutes to two hours, it is exposed to sulphuretted hydrogen, or one of the liquid hydrosulphurets. By these, various colours are produced upon the plate, according to the intensity with which Light has acted on the different parts.\* It must not be imagined, that the colours produced on the plate of copper are the natural colours of the object delineated. This colouration arises merely from the formation of films, of greater or less thickness, of sulphuret upon those parts of the ioduret of copper, which have been decomposed by the sun’s influence.

(294.) THE CHROMATYPE.—The first announcement of this process, was made by the author, in August, 1843. The process is so exceedingly simple, and the resulting pictures of so very pleasing a character, that, although it is not sufficiently sensitive for use in the camera obscura, it will be found of the greatest value for copying botanical specimens, engravings, or the like.

Good writing-paper is washed over with sulphate of

\* See the Repertory of Patent Inventions, October, 1841.



copper in solution, the strength of which is not of much importance; about one drachm to an ounce of water is preferred; when dry it is washed over with a moderately strong, but not a saturated, solution of the bichromate of potash. The paper, when dry, is fit for use, and it may be kept for a considerable time in a portfolio, without its sensibility being impaired.

When exposed to the sunshine, the first change is to a dull brown; and if checked in this stage of the process, we have a *negative* picture; but if the action of Light is continued, the browning gives way, and we have a *positive* yellow picture on a white ground. In either case, if the paper, when removed from the sunshine, is washed over with a solution of nitrate of silver, a very beautiful positive picture results. In practice it will be found advantageous to allow the bleaching action to go on to some extent: the resulting picture will be clearer and more defined than that which is procured when the action is checked at the brown stage. To fix these pictures, it is necessary to remove the excess of nitrate of silver, which is done by washing in pure water. If the water contains any muriates, the picture suffers; and long soaking in such water entirely obliterates it: if a few grains of common salt are added to the water, the apparent destruction is very rapid. The picture is, however, capable of restoration; all that is necessary being to expose it to good sunshine for ten minutes or a quarter of an hour, when it revives; but instead of being of a red colour, it becomes lilac, the shades of colour depending upon the quantity of salt used to decompose the chromate of silver. After this exposure, no fixing is required, the continued action of Light only still further improving the pictures.

(295.) Sir John Herschel has given some instances in which the chemical rays, as they are called, appear to destroy their own work. I am enabled to add another to the list. If a piece of the chromatype paper is exposed to the prismatic spectrum, it darkens instantly over the

region of the blue ray. This darkening extends to a point beyond the violet ray equal to the width of that ray, and downwards to the extreme edge of the green, proceeding, by long exposure, into the yellow. After a short time, this darkening is followed by a bleaching action, which commences at the upper edge of the violet, and proceeds slowly downwards to the edge of the most refrangible green. The brown over the green space gives way but very slowly; and it is only after very long-continued exposure to a good sun, that this portion is entirely whitened.

(296.) If we mix together a solution of sulphate of copper and of the bichromate of potash, the mixture will, in the dark, remain perfectly clear for a considerable time; but if exposed to sunshine, in a few minutes a rapid effervescence ensues, and a greenish yellow precipitate falls. This, and the precipitate produced in like manner in neutralised platina solutions, deserves the attention of chemists.

(297.) If to a solution of the sulphate of copper we add a solution of the chromate of potash — the neutral salt — a brown precipitate falls very copiously, which is a true chromate of copper. If this precipitate, after being well washed, is added to water rendered slightly sour by sulphuric acid, it is dissolved, and a solution is formed, which is, when spread upon paper, of a pure yellow. A very short exposure of the papers, washed with this solution, is quite sufficient to discharge all the yellow from the paper, and give to it a perfect whiteness. If an engraving is to be copied, we proceed in the usual manner; and we may either bring out the picture by placing the paper in a solution of carbonate of soda or potash, by which all the shadows are represented by the chromate of copper; or by washing the paper with the nitrate of silver. It may sometimes happen that, owing to deficient Light, the engraving is darkened all over when the silver is applied; this colour, by keeping, is gradually removed, and the

lights come out clear and sharp. The little excess of acid in the paper, acts upon the chromate, which has been partially changed, and a pale yellow, instead of a red salt, is formed.

(298.) If the chromate of copper is dissolved in ammonia, a beautiful green solution results. If papers are prepared with this solution, they act similarly to those last mentioned. If the pictures prepared as above (297.), are washed with ammonia, they are nearly obliterated; but upon exposing them to the air and Light, negative pictures of a pale blue colour result. If a neutral solution of the chloride of gold is mixed with an equal quantity of the bichromate of potash, and paper, being washed with solution, is dried near the fire; on exposing this paper to light, it speedily changes, first to a deep brown, and ultimately to bluish black. If an engraving is superposed, we have a negative copy, blue or brown, upon a yellow ground. If this photograph is placed in clean water, and allowed to remain in it for some hours, very singular changes take place. The yellow salt is all dissolved out, and those parts of the paper left beautifully white. All the dark portions of the paper become more decided in their character, and accordingly as the solarization has been prolonged, or otherwise, or the Light has been more or less intense, we have either *crimson, blue, brown, or deep black negative photographs*, of a most beautiful character.

(299.) IODIDE OF COPPER, by long exposure, does not appear to undergo any change; if, however, it is washed over with nitrate of silver, it becomes unequally black upon the exposed and covered parts. If, previously to exposure, freshly made iodide of copper is washed over with nitrate of silver, an intense black paper results. This paper has some remarkable properties: if it is exposed wet to the prismatic spectrum, a bleaching action comes on with rapidity under the red and orange rays, particularly over the space occupied by the "parathermic" rays. Little or no action is seen to take place over any other

part; but upon removing the paper from the Light, and washing it with hyposulphite of soda, it becomes evident that a deep browning, penetrating quite through the paper, has been effected by the blue rays.

If we place leaves of tolerable transparency upon such a paper, the bleaching action is carried on beneath them, whilst the exposed parts remain of a jet black colour.

(300.) All the salts of copper undergo some change under the influence of the solar radiations. If a solution of any salt of copper is laid over paper, and it be exposed to the sunshine, a change is brought about; and if, after it is removed from the sunshine, it is washed with nitrate of silver, the covered portion remains of its original colour, whilst the exposed parts darken very considerably. I do not doubt but by attention and experiment, some of the cupreous salts may afford very valuable photographic preparations. At all events these results, to which I was the first to call attention, show the immense field of inquiry which waits some cautious investigations.

(301.) MANGANESE.—The instability of some of the salts of manganese, led to the hope that this metal might be made available for photographic processes. Although this has not yet been effected, a sufficient amount of evidence of its compounds being, like those of other metals, susceptible of change under solar influence, has been obtained.

(302.) If two bottles are filled with a solution of mineral chameleon (manganesiate of potash), and one of them be placed in the sunshine, whilst the other is carefully preserved in darkness, it will be found that the solution exposed to the sun, will very rapidly throw down a deep brown precipitate, whereas the one in the dark, remains for some time quite clear. This experiment, if cautiously made in weak diffused day-light, will exhibit, although more slowly, the same change, showing in a very remarkable manner the influence of the solar rays in determining the tendency to precipitation.

(303.) If a solution of the manganesiate of potash is washed over paper, it imparts to it a brown colour. The sun's rays have a tendency to discharge this colour, and thus give a positive image. The addition of a small quantity of the nitrate of silver to paper prepared with this salt of manganese, renders it brown, but upon exposure it assumes a very intense blackness.

(304.) If the deutoxide of manganese is dissolved in a solution of the cyanuret of potassium, and paper washed with this solution, it will be found that an exposure to sunshine for half an hour, will produce no visible change over the surface; but on looking through the paper, it becomes evident that a considerable deposition of a brown precipitate has taken place within its pores over the spaces which were not protected from the action of the solar rays.

(305.) Many of the salts of manganese, spread upon paper, exhibit some evidence of change under solar action. The muriate in particular undergoes decomposition, and some oxide of manganese is deposited. It is, however, to be remarked, that in those cases in which no apparent change is produced even by prolonged exposure to the sun's rays — that is, no change of colour — we are not to conclude that no disturbance has taken place. In nearly all cases it will be found that a sufficient amount of change has been effected to be rendered evident by the application of some reagent. In particular, in the instances of the manganesic salts, as in those of copper, the subsequent application of the nitrate of silver produces very decided evidences of change. The chloride of gold, in some cases, appears to be reduced by these salts which have undergone solarization, in a manner strikingly different from the effect produced by salts which have not been exposed to the sun. It has also been noticed that the balance of affinity has been so much disturbed by the solar agency, that ammonia, the hydrosulphurets, and the ferroprussiates, produce different effects upon the

exposed and covered parts. May not these very curious phenomena be dependent upon the absorption of the active principle which is found to exist in the sun's rays, and every radiant source?

(306.) LEAD.—The puce-coloured oxide of lead, in a moist state, under the influence of the sun's rays, parts with oxygen, and is converted into the deutoxide. It has been found that this is more decidedly the case with the oxide prepared by chlorine from the acetate of lead than with that which is prepared by the action of nitric acid on minium or red lead; from which it would appear that the oxygen is in looser combination in the one case than in the other. It was observed by Sir H. Davy, that this change was effected by the least refrangible rays; hence we may suppose it to depend on the calorific rays rather than the chemical rays.

(307.) In a very early stage of his photographic inquiries, Sir John Herschel was led to employ mordant washes of lead, and of organic matter precipitated by lead. These were found to have a very decided effect in quickening the change which takes place upon the nitrate of silver when exposed to sunshine; and in some cases it was found that a sensibility quite equal to that of the processes proposed by Mr. Talbot was produced. Papers, unfortunately, which are prepared with lead, have a tendency to darken spontaneously, or at least to turn very yellow, or sometimes grey, in the dark.

(308.) If red lead is boiled with cyanide of potassium, and paper washed with this solution is exposed to the Light, it undergoes some change, which is rendered evident by nitrate of silver. If gallic acid is washed over paper saturated with this solution, it becomes at first pink, and then brown. Upon exposing this to the sun, it loses colour; but although this change is produced with some rapidity, it is not found to proceed on to the point of whiteness, however long the paper may be exposed to sun-

shine. If acetate of lead is washed over a paper, and then a weak solution of gallic acid, it will be found that no change of colour is produced for some time in perfect darkness; but a very short exposure to Light brings on a very decided darkening, which goes on even without the continuance of the solar influence. Numerous combinations of lead and other metals have been examined, with a view to detect, if possible, some of those cases of unstable affinity which yield the most interesting photographic results. Lead certainly has the power of increasing the liability of gold and platinum to change, and of carrying on the degree of darkness ultimately produced, much further than when these metals are used alone; and hence it is very probable that lead may in some processes be of considerable use, where the object is to produce originals from which a great number of transfers may be taken.

(309.) NICKEL.—The salts of this metal, spread upon paper, pass slowly into a fine light brown, giving tolerably good negative pictures. Nitrate of nickel, spread upon paper, and then washed with ammonia, affords some very interesting photographic results. It is difficult to decide upon the exact proportion in which the ammonia should be used. It appears that a sufficient quantity should be applied to effect the precipitation of the oxide of nickel, but not enough to re-dissolve it. If an excess of ammonia is employed, the paper appears absolutely insensible; but if the proportions are well adjusted, a preparation which darkens quite as readily as the nitrate of silver, results. The subsequent application of the nitrate of silver considerably darkens the parts which have been already changed by Light.

(310.) Upon submitting paper thus prepared to the prismatic spectrum, it was found that the change was entirely dependent upon the influence of the rays of greatest refrangibility, the prolonged action of the other rays producing no apparent effect.

(311.) **TIN.**—It has been found that chloride of tin, carefully neutralised, will, when in contact with any organic matter, undergo a considerable change in the sunshine; a dirty appearance being given to it in half an hour, so as to contrast very decidedly with the original whiteness. Its oxide, washed, after exposure to the sun, with nitrate of silver or chloride of gold, exhibits very decided evidences of change.

The purple of cassius changes in the sunshine to a steel grey. If the dyers' muriate of tin is applied to paper, and then dried without much heat, it may be used to produce results of some interest. If, after exposure for half an hour to good sunshine, the paper is washed with very dilute chloride of gold, the purple of cassius will be formed with much greater readiness over the shaded than the exposed parts, giving thus positive images. If the solution of gold is applied too copiously, the darkening is carried on with great rapidity over the whole of the sheet; but although at first it appears that the sheet is of one uniform colour, it will, by keeping, show distinctly the covered spaces.

(312.) **COBALT.**—The changes which some of the salts of this metal undergo when exposed to heat are well known. These appear to depend entirely upon the abstraction of moisture. Under the influence of the prismatic spectrum, these changes of colour take place, but only under the red rays, by long exposure. Another kind of change is apparent under the spaces on which the blue rays fall, and which, very different from that produced by the heat rays, is permanent. On paper the nitrate, muriate, and carbonates of cobalt, have been found to deepen in colour very considerably under exposure. In a few instances, when the sun has been very fervent, the pale blue of these salts changed to a good violet; but when removed from the light, this colour passes into a deeper blue. Washed with nitrate of silver, the blue



passes into a brown; and if again exposed, positive images are produced.

(313.) The very intense and beautiful brown which is given to the ordinary argentine preparations, by the presence of cobalt, may possibly be of some advantage in practice. If paper is washed with muriate of cobalt, and then nitrate of silver, in proper proportions to allow the silver to be in excess, it will be found to be superior to the ordinary muriated papers; and it is so far economical, that a very much weaker solution of the nitrate of silver may be used, and as deeply coloured an impression made as when a larger dose of the silver has been applied. Nitrate of silver does not darken very readily when spread on paper; but if mixed with nitrate of cobalt, it will be found to change more easily, and give a deeper colour than the silver salt alone would do.

(314.) ARSENIC. — Some of the arsenical combinations will be found to be influenced by the solar rays, and particularly the arseniate of potash. If a paper washed with this salt is exposed for an hour or two, the subsequent application of nitrate of silver brings out an image of any body used to obstruct the Light.

(315.) Bismuth, Cadmium, Rhodium, and some other metals, have been found, under certain conditions, to afford evidence of the same kind of changes as we have seen takes place in so many other bodies. The attentive study of the peculiarities of the rarer metallic compounds will, it appears, probably afford many curious results. As far as my researches have been carried, they afford good presumptive evidence that every chemical combination undergoes some peculiar modification when exposed to the power of the solar rays.

(316.) CHROMIUM. — The bichromate of potash is particularly distinguished by its photographic properties. These were first pointed out by Mr. Mungo Ponton, who proposed the following interesting process: — Well-sized

paper is to be immersed in a solution of bichromate of potash, and dried by the fire; by this it assumes a fine yellow colour, and it may be kept for any length of time without injury, and is always ready for use. When an engraving is laid on this paper, and it is exposed to the sunshine, it passes rapidly, over all the parts through which the rays can act, into a light brown; consequently the first result is a yellow picture upon a brown ground. In this state the photograph cannot be exposed to the Light, as all the yellow parts would become brown. If, however, the paper is soaked in water, all the unchanged salt is dissolved out, but that which is browned is not disturbed. We have thus a delicate negative picture, from which positive copies may be taken. If the paper is exposed too long to sunshine, it loses colour. A pleasing variety may be made by mixing sulphate of indigo, with the bichromate of potash, the colour of the object and of the ground being different shades of green.

(317.) The change which the solar rays produce upon this salt is one of deoxidation. Chromic acid is liberated, and it combines with the organic matter of the size of the paper. Mr. Ponton states that the neutral chromate exhibits no such change; it has, however, been since discovered that even the chromate of potash on paper will darken; but it is only by long exposure that much effect can be produced; and the ultimate degree of darkness falls very far short of that given by the bichromate. This change is effected by the blue rays of the spectrum, and their action appears to be confined within rather narrow limits.

(318.) M. E. Becquerel has investigated, with considerable care, the action of chromic acid on organic bodies under the influence of Light, and he has shown that the darkening is dependent upon the nature of the size used on the paper. It occurred to him, therefore, that by the application of starch as a size to the paper, pleasing

effects might be produced by the agency of iodine, and the result was satisfactory. According to Becquerel's method, a sizing of starch is applied very evenly over the paper; it is then steeped in a concentrated solution of the bichromate of potash, and dried. Pictures are taken in the usual way, and the paper is washed and dried. When dry, it is immersed in a weak alcoholic solution of iodine, and afterwards, when it has remained in it for some time, it is rinsed in water, and carefully dried between folds of blotting paper. If the drawing is not considered to be sufficiently distinct, the immersion may be repeated until it becomes so. The effect is not improved by using a more concentrated solution of iodine. When the paper is wet, the shades of the picture are of a very fine blue; but when it is dry, they become of a deep violet. If, while the photograph is still wet, it be covered with a layer of gum-arabic, the colour of the drawing is greatly preserved, and it is more beautiful when dry.

(319.) The metallic chromates have been thought to be compounds of too permanent a character to change under solar influence. Many of them, however, deepen in colour by exposure; and the chromate of mercury has been found to undergo a very remarkable change. Paper was prepared with the bichloride of mercury (corrosive sublimate) and the chromate of potash, and exposed with an engraving upon it for some hours. There was evidently some change of colour, but it was very slight, over the exposed parts. This was placed aside, and remained in a dark drawer for two or three months without being noticed. It was then found to have become through its substance semi-metallic, and, both on the front and back of the paper, a tolerably good impression of the engraving was visible.

(320.) FERROCYANIDES. The photographic uses of these salts have already been the subject of consideration (140.); and it only remains to state, in this place, that

a solution of the ferrocyanide of potassium mixed with a solution of the iodide of potassium, applied to paper, speedily changes in the sunshine, and may be used for the production of a very pretty variety of negative photographs. M. Fischer pointed out that a solution of ferrocyanide of potassium precipitated by alcohol, and rapidly dissolved in water, when exposed to Light passes into a green and then a blue colour, depositing Prussian blue, and giving a strong smell of hydrocyanic acid.

## CHAPTER V.

## ON THE ACTION OF THE SOLAR RAYS ON NON-METALLIC SUBSTANCES.

(321.) RESINS.—*Heliography*.—By this name M. Niepce distinguished, in 1827, the first process by which the images of the camera obscura were rendered permanent, after having impressed themselves upon prepared tablets. Although the process of the philosopher of Chalons is not likely to attract much attention from the photographer, who is now in possession of processes which infinitely surpass it in sensitiveness, yet, as it develops some important operations of the solar rays, it could not be allowed to pass without notice. This process is now becoming more important, since it is employed for the purpose of obtaining impressions upon metal plates and lithographic stones, which can be etched, or prepared for printing. M. Niepce has given directions, which are essentially as follows:—

(322.) Into a glass is put a small portion of asphaltum, upon which is dropped essential oil of lavender till the asphaltum is impregnated with it, and as much additional oil is added as will cover it to a slight depth. The mixture is then submitted to a gentle heat, until the whole of the essential oil is saturated with the colouring matter of the bitumen. A highly polished plate of silver is procured, and with a soft roll of skin some of this varnish is applied, in a very thin and equal coating; the plate is then placed upon heated iron, and when the varnish has ceased to simmer, it is withdrawn, and left to cool and dry in a gentle temperature, secured against any moisture. The plate thus prepared is placed in the camera,

and in bright summer sunshine a period of four or six hours is necessary to produce anything like the proper effect. The images are exceedingly faint at first, but they are brought out by the action of a solvent, which removes from the plate, or renders perfectly transparent, those parts upon which the solar rays have not acted. This solvent consisted of one part, by volume, of essential oil of lavender, poured upon ten parts, by measure also, of oil of white petroleum. The varnished tablet is placed in a proper vessel, which has been filled with the solvent, and the operator, by reflected Light, watches the development of the images, and removes the plate when the proper effect is produced.

The process is then completed, by placing the plate upon an inclined plane, and washing it with very clean water, to remove all the softened parts of the varnish which may still adhere to it. This varnish may be spread upon metal, glass, or stone. Engravings are more easily copied by this method than pictures from nature can be procured.

(323.) Niepce appears to have advanced this process considerably; but his partner in this inquiry, M. Daguerre, suggested the use of materials by which the operation was greatly improved, as it regards sensitiveness and general effect. These improvements consisted in applying the residuum obtained by the evaporation of the essential oil of lavender to the plates, instead of the asphaltum; and instead of dipping the plate, after exposure, into a solvent, it is so placed that the *vapour* of petroleum acts upon it, by which the portions of the varnish that have been acted on by the Light are rendered transparent.

(324.) Daguerre remarks that all bitumens, all resins, and all residua of essential oils, are decomposable by sunshine in a very sensible degree. To exhibit this action, very thin coatings of them should be spread over fitting surfaces; and it is a curious fact, and well worthy the inquiry of chemists, that different solvents act differently

upon these resinous plates after they have undergone the action of solarization. If alcohol is used, the parts on which the Light acted are dissolved off; but if an essential oil is employed, the parts in shadow are those effected by the solvent.

I have tried nearly all the gum resins in general found in the shops of druggists, &c., and these are, I find, acted upon in the same way as the pure resins, and indeed the gums give some indications of losing or acquiring solubility by exposure to sunshine.

(325.) **GUAIACUM.** — The colour of this peculiar resin is yellowish brown, but upon exposure to the sun's rays it becomes green. Dr. Wollaston first pointed out that this change was brought on by the violet rays; that the original colour was restored if it was exposed to the red rays, and that the same change was effected by the application of artificial heat.

Dr. Wollaston did not observe any change on exposing pieces of card, covered with an alcoholic solution of this gum, in the prismatic spectrum. But, taking a lens of seven inches in diameter, and having covered the central part of it, so that a ring of one-tenth of an inch only was left at its circumference, he could collect the rays of any colour in a focus—the focus for yellow Light being  $24\frac{1}{2}$  inches. By this arrangement it was found, as above stated, that the violet and blue rays changed it to green, that the yellow rays produced no effect, and that in the red rays the *green colour* was destroyed. When the guaiacum was placed in carbonic acid, it could not be rendered green at any distance from the lens, but was rapidly restored from green to yellow by the red rays. Thence he inferred that the rays of greatest refrangibility favour disoxygenation, but that the least refrangible ones favour oxygenation. These changes have been investigated by Sir John Herschel, the results of whose inquiries I shall now give.

(326.) This resin dissolved in alcohol, spread evenly

upon paper, gives nearly a colourless ground. Exposed to the spectrum, a blue colour is impressed upon the paper, over the spaces between the least refrangible green rays, and a point situated upon the invisible rays a few lines beyond the violet rays. The action of dispersed Light changes the paper to a pale green; but over the region of the red rays the original pale colour of the paper is preserved.

(327.) If a paper thus prepared is exposed to the action of the solar rays, which have permeated a deep blue fluid, until it assumes a uniform pale blue tint, it will be found, that under the influence of the prismatic spectrum, a restoration of the original yellow colour takes place over the region of the green, yellow, orange, and red rays, the blue colour being entirely removed by the orange ray. It will be remembered that Dr. Wollaston attributed this restoration of colour to the action of heat. Had this been the true interpretation, we might expect to find the change most evident in that part of the spectrum where the heat was greatest, which we see is not the case.

(328.) Sir John Herschel exposed a portion of this paper to the action of chlorine considerably diluted with common air, by which it acquired a pale, dirty, greenish-yellow hue. Transferred immediately to the spectrum, it was impressed with faint tints nearly corresponding to the natural ones: the red was evident, the yellow dilute, and nearly white; the blue, a fine sky blue; while beyond the violet succeeded a train of somewhat greenish darkness.

(329.) If a paper prepared with the alcoholic solution of guaiacum, is placed in an aqueous solution of chlorine, it acquires a beautiful and pure celestial blue colour. "This paper is very sensitive, and may be used for copying engravings, which it does with this singularity, that the picture penetrates the paper, and appears on the back with nearly the same intensity as on the face." Under



the influence of the less refrangible rays, the blue colour is changed into a pale reddish yellow, but simply whitened over the more refrangible region of the spectrum. Photographs or spectra received on this paper speedily fade. (*Herschel.*)

(330.) Several experiments were tried, with a view of determining if the conclusions arrived at by Dr. Wollaston, as to the influence of artificial heat in producing these changes of colour were correct, and if they explained the restoration produced by the least refrangible rays of the solar spectrum. It has already been noticed that the rays of greatest calorific power produce no change upon the paper, whereas the decoloration is brought about by the rays in the region of the red, orange, yellow, and green spaces. It was found by Sir John Herschel that an artificial heat between the limits of  $180^{\circ}$  and  $280^{\circ}$  soon changed guaiacum from a green to a yellow state if moist, but that no such change was produced if absolutely dry. It was thought desirable to try the effect of the spectrum upon papers prepared as above, whilst, at the same time, they were subjected to a temperature sufficiently high to produce this effect had the paper been moist; this artificial heat being meant to assist the power of the calorific rays: this was done by holding a hot iron at the back of the paper. It was found, however, that, although it quickened the action over the luminous spaces, which were not at all changed in their character, that no perceptible effect was produced by those rays which possess the greatest heating power. From these researches it would appear that this restoration of guaiacum to its original colour is not dependent upon the heating power of the sun's rays, but upon some influence strictly analogous to that exerted by the "chemical rays," but modified by the combined influences of Light and heat.

(331.) COLOURED JUICES OF FLOWERS. — The action of Light on the juices of plants has been carefully studied by M. Chevreul; but as his experiments were made with

reference only to their permanence as dying materials, and with white Light as it proceeds from the sun, they afford no information as to the influence of the separated rays. This subject has alone engaged the attention of Sir John Herschel and Mrs. Somerville.

(332.) Certain precautions are necessary in extracting the colouring matter of flowers. The petals of fresh flowers, carefully selected, are crushed to a pulp in a marble mortar, either alone or with the addition of a little alcohol, and the juice expressed by squeezing the pulp in a clean linen or cotton cloth. It is then to be spread on paper with a flat brush, and dried in the air without artificial heat. If alcohol be not added, the application on paper must be performed immediately, as the air (even in a few minutes) irrecoverably changes or destroys their colour. If alcohol be present, this change is much retarded, and in some cases is entirely prevented.

(333.) Most flowers give out their colouring matter to alcohol or water. Some, however, as the *Escholzias* and *Calceolarias*, refuse to do so, and require the addition of alkalies, others of acids, &c. Alcohol has, however, been found to enfeeble, and, in many cases, to discharge altogether these colours; but they are, in most cases, restored upon drying, when spread over paper. The juice of the *Viola tricolor*, extracted by alcohol, is a striking example of this temporary destruction of colour. Papers tinged with vegetable colours must be kept perfectly dry and in darkness.

(334.) The colour of a flower is by no means always, or usually, that which its expressed juice imparts to white paper. The red damask rose, called by florists the black rose, gives a dark slate blue, as do also the clove carnation and the black holyoak; and the common red poppy (*Papaver Rhæas*) imparts to paper a rich and most beautiful blue colour. Sir John Herschel attributes these changes to the escape of carbonic acid in some cases; to a chemical alteration, depending on the absorption of

oxygen, in others; and again in others, especially where the expressed juice coagulates on standing, to a loss of vitality, or disorganisation of the molecules. To secure an evenness of tint on paper, the following manipulation is recommended:—“The paper should be moistened at the back by sponging and blotting off. It should then be pinned on a board, the moist side downwards, so that two of its edges (suppose the right-hand and lower ones) shall project a little beyond those of the board. The board then being inclined twenty or thirty degrees to the horizon, the alcoholic tincture (mixed with a very little water, if the petals themselves be not very juicy) is to be applied with a brush in strokes from left to right, taking care *not to go* over the edges which rest on the board, but *to pass* clearly over those that project; and observing also to carry the tint from below upwards by quick sweeping strokes, leaving no dry spaces between them, but keeping up a continuity of wet spaces. When all is wet, cross them by another set of strokes from above downwards, so managing the brush as to leave no floating liquid on the paper. It must then be dried as quickly as possible over a stove, or in a current of warm air, avoiding, however, such heat as may injure the tint.”

(335.) Before I proceed to give Sir J. Herschel's remarks on the results of his inquiries, I shall mention, as briefly as is consistent with a correct understanding of the matter, several of the most remarkable results obtained by him upon vegetable juices, referring all those who may desire more detailed information to his memoir itself.\*

(336.) *Corchorus Japonica*. — The flowers of this plant impart a fine yellow colour to paper. Sir John Herschel says he has met with no vegetable colour so sensitive as this. If the flowers are gathered in the height of their season, paper coloured with them begins to discolour in ten or twelve minutes in clear sunshine, and in half an hour is

\* On the Action of the Rays of the Solar Spectrum on Vegetable Colours, &c. “Philosophical Transactions, Part II. for 1842.”

completely whitened. The colour seems to resist the first impression of the Light, as if by some remains of vitality, which being overcome, the tint gives way at once, and the discoloration, when commenced, goes on rapidly. *It does not even cease in the dark when once begun*; hence photographic images received upon papers prepared with this juice slowly fade out.

(337.) *Prismatic Analysis*.—Exposed to the spectrum, in about fifteen or twenty minutes the colour is totally destroyed, and the paper whitened in the whole region of the green, blue, and violet rays, to which, therefore, the most energetic action is confined. If the action of the spectrum be prolonged, a much feebler whitening becomes sensible in the red, and a trace of it also beyond the violet into the “lavender” rays. By keeping papers thus impressed, terminal spots were detected beyond the red extremity, and also beyond the violet, they having gradually developed themselves.

(338.) *Common Ten-weeks' Stocks*.—*Mathiola annua*.—The colour imparted to alcohol by the double variety of this flower, in the height of its flowering, is a rich and florid rose red; when fresh prepared, papers stained with it are sensibly discoloured in a few hours, and completely whitened in two or three days. Exposed to the spectrum, the rays chiefly active in operating the discoloration, are found to be those extending from the yellow to the less refrangible red, beyond which rays the action terminates abruptly. Above the yellow, it degrades rapidly to a minimum in the blue, beyond which it recovers somewhat, and attains a second but much feebler maximum in the violet rays.

(339.) Sulphurous acid whitens this paper, but it resumes its original colour after a little time, which is materially quickened by the aid of Light. Papers thus completely discoloured, when exposed to the spectrum, were restored to their original colour, *by rays complementary to those which destroy it in the natural state of the*

*paper*; the violet rays being chiefly active, the blue almost equally so, the green little, and the yellow, orange, and most refrangible red not at all. Sir John Herschel attributes, and I think rightly so, the power of the sulphurous acid in inducing a dormant state of the colorific principle to a partial deoxidisement, unaccompanied, however, with disorganisation of its molecules.

(340.) It has been noticed that alcohol in many cases weakens the colours of vegetable juices, and in some entirely masks them. With the *Papaver orientale* this is very strikingly shown. The colour of the flower is a brilliant orange, "the colouring matter of which is only extractable by alcohol, and then only in a state so completely masked, as to impart no more than a faint yellowish or pinkish hue to paper, which it retains when thoroughly dry, and apparently during any length of time, without perceptible increase of tint." This paper is immediately rendered a vivid scarlet colour when an acid is applied to it. If paper covered with this alcoholic extraction is exposed for a long period to the influence of the Light, it undergoes some disorganisation, so that, on being exposed to the vapours of muriatic acid, a dormant picture — supposing it to have been covered with an engraving — is gradually developed in a soft and pleasing style. The time required to produce these pictures extends over from twenty to thirty days.

(341.) Papers covered with an alcoholic tincture of *turmeric* are slowly acted upon. It is whitened by the blue and violet rays. If it is browned by carbonate of soda it is somewhat more sensitive, especially when wet, and an abruptly terminated action is perceptible in the red region.

(342.) *Bulbine bisulcata* and two other species from the Cape of Good Hope were found by Sir John Herschel to yield from the green epidermis of their leaves and flower stalks a bright yellow juice, which darkens rapidly on exposure to Light, changing at the same time to a ruddy

brown. Exposed to the spectrum, the less refrangible rays are found inoperative either in inducing a change of tint, or in preserving that portion of the paper on which they fall from the influence of dispersed Light. A darkening commences about the mean yellow ray, but it continues very feeble through the green ray, above which it darkens more strongly, arriving at its maximum in the blue, but extending to a considerable distance beyond the violet with some degree of intensity.

(343.) *Cheiranthus cheiri*, *Wallflower*. — “A cultivated double variety of the flower, remarkable for the purity of its bright yellow tint, and the abundance and duration of its flowers, yields a juice, when expressed with alcohol, from which subsides, on standing, a bright yellow finely divided fæcula, leaving a greenish-yellow transparent liquid, only slightly coloured supernatant. The fæcula spreads well on paper, and is very sensitive to the action of Light, but appears at the same time to undergo a sort of chromatic analysis, and to comport itself as if composed of two very distinct colouring principles, very differently affected. The one on which the intensity and sub-orange tint of the colour depends, is speedily destroyed, but the paper is not thereby fully whitened. A paler yellow remains as a residual tint, and this on continued exposure to Light, so far from diminishing in tone, slowly darkens to brown. Exposed to the spectrum, the paper is first speedily reduced nearly to whiteness in the region of the blue and violet rays. More slowly, an insulated solar image is whitened in the less refrangible portion of the red. The exposure continuing, a brown impression begins to be perceived in the midst of the white streak, which darkens very slowly over the region between the lower blue and the extreme violet rays. It never attains any great intensity, but presents a singular appearance in the midst of the white train previously eaten out.”

(344.) The common *Marigold* yields an insoluble fæcula, which appears identical with that produced by the wall-

flower and that of the *Corchorus japonica*, and it is found to be quite as sensitive to Light; but photographs procured upon it cannot be preserved, the colour is so fugitive. The juice of the *Mimulus Smithii* affords a yellow dye, which is similarly affected. "The *Ferrarea undulata*, a dark-brown flower, yields, when expressed, a dull green juice, which, spread on paper and dried, turns very speedily blue, under the influence of the blue and violet rays of the spectrum, owing to the destruction of this yellow principle, which, mingling with the substratum of blue (itself a much more indestructible tint), gives its natural tinge of green. The brown colour of the French marigold, *Tagetes patula*, passes rapidly in sunshine from brown to green, probably from the destruction of the same yellow principle. And bees' wax, it is well known, is bleached by Light, from the presence of a similar fugitive principle.

(345.) The *Viola odorata* yields to alcohol a rich blue colour, which it imparts in high perfection to paper. Exposed to sunshine it fades pretty rapidly, but a residual blue tint remains, which resists the action of Light for a long time, even for weeks. When carbonate of soda is added to this solution it becomes green, and a slip of paper stained with this fluid, exposed to the spectrum, is changed yellow under the orange and red rays; a slight discoloration is perceived in the indigo-blue rays, but not the slightest alteration under the *green* rays. The colouring matter of the purple iris shows this in a still more marked manner. In these instances the blue constituent of the green is destroyed by the solar rays. (*Herschel.*)

(346.) A variety of *Sparaxis* from the Cape of Good Hope gave to paper a dark olive-green colour, which was nearly insensible to Light. The addition of carbonate of soda changes this colour to a good green, which is tolerably sensitive to solar influence. A photograph impressed on a paper prepared with it is reddened by muriatic acid fumes. If then transferred to an atmosphere of ammonia, and when supersaturated, the excess of

alkali allowed to exhale, it is fixed, and of a dark-green colour. (*Herschel.*)

(347.) *The Red Poppy.*—*Papaver Rhæas* yields a very beautiful red colour, which is entirely destroyed by Light. When perfectly dried on paper the colour becomes blue. This blue colour is speedily discharged by exposure to the sun's rays, and papers prepared with it afford very interesting photographs. The purple juice of the *Senecio splendens*, the double purple groundsel, imparts a beautiful colour to paper. It requires, however, an exposure of some weeks to daylight before the original whiteness is restored, which it at length is in the most perfect manner.

(348.) The juices of the leaves of a great number of plants have been examined by the author; and the juices from leaves of the laurel, the vine, the common cabbage, and the grasses, have been found to be sufficiently sensitive, when spread upon paper, to give very good copies of engravings in an hour, provided the atmosphere was clear and the sun bright. The action of the prismatic spectrum upon those I have examined, agrees very nearly with results published by Sir John Herschel, as obtained upon the juice of the elder leaf. The red rays have a decided action, and give a ruddy yellow impression. It appears to me, this change is dependent upon the calorific agency merely, as similar changes are brought about by artificial heat. On the upper edge of the yellow ray, the space between the red and it being unaffected, a very faint image begins to be formed; this action goes on increasing up to the mean blue rays; it then declines, and ceases altogether within the limits of the visible violet ray.

(349.) From an examination of these researches on the colouring matters of plants, it will be seen that the action of the sun's rays is to destroy the colour, effecting "a sort of chromatic analysis, in which two distinct elements of colour are separated, by destroying the one and leaving the other outstanding." The action is confined within the visible spectrum, and thus a broad distinction is exhibited.



between the influence of the sun's rays on vegetable juices and on argentine compounds, the latter being most sensibly affected by the "invisible rays" beyond the violet.

(350.) "It may also be observed, that the rays effective in destroying a given tint are, in a great many cases, those whose union produces a colour complementary to the tint destroyed, or, at least, one belonging to that class of colours to which such complementary tint may be referred. For example, yellows tending towards orange are destroyed with more energy by the blue rays; blues by the red, orange, and yellow rays; purples and pinks by yellow and green rays."

(351.) I may here mention, that some very remarkable changes take place in the colours of many vegetable powders, in which we might least expect such alterations to occur. Experience has shown to the pharmacopolist the necessity of preserving the powdered leaves of the foxglove, the hemlock, the henbane, the aconite, and other green vegetable powders of active medicinal powers, in the dark. It is found that these powders do not merely lose colour, — passing slowly from a green into a slaty grey, and ultimately into a dirty yellow, — but they undergo some decomposition, by which, at the same time, they lose much of their medicinal activity, and indeed after a season they become nearly inert.

(352.) Few pharmaceutical articles suffer more in this respect than the powder of the jalap root; the ipecacuanha also loses much of its emetic power by exposure to Light. This is entirely independent of any action of the air or moisture. I have observed these deteriorating influences on those powders, which have been kept in the most carefully closed bottles.

(353.) The powders of Cascarilla bark, of the Valerian root, and some others, particularly some of the varieties of rhubarb and the ginger root, are found to adhere with considerable firmness to the sides of the bottles next the Light, whereas the sides in shadow are left clear. I have also observed that a deposit will take in a similar manner on the

sides of bottles containing some of the vegetable tinctures. This of course depends upon the same function which occasions camphor to be deposited in crystals upon the side of the glass next the Light, and maintains them there; whereas, if that side is turned from the Light, the crystals will be gradually removed and again deposited on those parts upon which the rays of Light first impinge. These phenomena must have been long and often observed, yet we have not any satisfactory explanation of them. It does, however, appear, that we are advancing gradually towards the elucidation of these and many other matters, which have often excited the wonder of observers without leading to any particular inquiry.

(354.) In the "Philosophical Transactions for 1844" is published an extract of a letter from Mrs. Somerville to Sir J. F. W. Herschel, dated Rome, September 20. 1845: On the Action of the Rays of the Spectrum on Vegetable Juices.

There is so much that is curious in this communication, that I have extracted a portion to show the character of the investigations in which that lady is engaged.

"In the following experiments the solar spectrum was condensed by a lens of flint glass of  $7\frac{1}{2}$  inches focus, maintained in the same part of the screen by keeping a pin-hole, or the mark of a pencil, constantly at the corner of the red rays, which were sharply defined by using blue spectacles to protect my eyes from the glare of light, and the apparatus was covered with black cloth in order to exclude extraneous light.

"Thick white letter paper moistened with the liquid to be examined, was exposed wet to the spectrum, as the action of the coloured light was more immediate and more intense than when the surface was dry. As I had not access to the morning sun, the observations were made between noon and three in the afternoon."

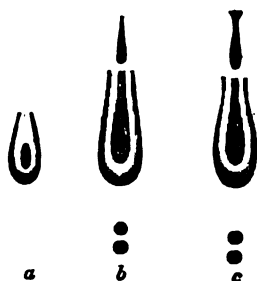
(355.) Mrs. Somerville approached very near to the discovery of the extra spectral rays of Stokes, as the following paragraph shows.

“ The lavender rays came vividly into view; under a condensed spectrum, on white paper washed with a solution of sulphate of quinine in dilute sulphuric acid, they were narrow, and their length by rough measurement was equal to the distance between the upper edge of the violet and the lower edge of the blue. They were very brilliant on black silk or other dark surfaces, and invariably of lavender colour; and even on paper stained with turmeric, the pale yellow rays which you had observed were tipped with lavender, on being washed with this liquid, though its duration was momentary, as it vanished as the surface became dry; but they were permanent in other instances.

(356.) “ The lavender rays changed their colour with a change of the liquid; for instance, they are lavender colour on nitrate of silver discoloured by Light to a very pale brown, washed with a solution of sulphate quinine in dilute sulphuric acid; whereas, on a similar surface of pale brown nitrate of silver washed with the juice of the petals of the pale blue *Plumbago auriculata*, in distilled water, to which sulphuric acid was added, they appeared of a vivid apple green, and acquired a tip of lavender colour, on the surface being washed with a solution of sulphate of quinine in dilute sulphuric acid of considerable strength. The effect, however, was transient. After several unsuccessful attempts to repeat this experiment next day, I at length discovered that its success depended upon the acid being strong enough to decompose the juice and give it a reddish orange hue, and even then the rays are not vivid till the paper has been frequently washed with the juice and become nearly dry; and the experiment is more successful when the liquid has been kept a night. The action of the surface in changing the colour of the lavender rays may be illustrated by passing the spectrum over paper coated with nitrate of silver brought to a clear yellow brown by exposure to the sun, one half washed by the liquid in question, and the other half with a solution of sulphate of

quinine in dilute sulphuric acid. On the first half the lavender rays became vivid apple green, while, on passing to the other half, they instantly changed to a equally vivid lavender colour. These rays often darken the surface throughout their whole length; sometimes they acquire a powerful bleaching action, and sometimes they have no effect, as evidently appears from the following experiments.

(357.) "The juice of fresh-gathered petals of *double flowering pomegranate* in alcohol afforded an example of this. Paper washed with this juice became rich crimson, and on being exposed wet to the condensed spectrum, a narrow line of deep crimson was formed at the junction of the green and yellow rays, or perhaps in the most refrangible yellow, surrounded by a whitish lozenge-shaped border (*a*). On again washing with the juice, instead of the white border, which had vanished, there was a crimson flame-shaped image, curved at the lower edge of the yellow rays, and tapering upwards to the violet; its colour was darker than that of the ground, though paler than the narrow line which maintained its intensity; and although the latter increased in width, it did not become as broad as the image in question. At the upper end of the violet another little dark image was formed, apparently owing to the action of the lavender rays, having exactly their form: the orange and red rays, especially the red, had no effect, though at the distance of about half the length of the spectrum beyond the red, two distinct spots were formed of deep crimson, which I believe to be the heat spots which you discovered. After some time a bleaching appearance surrounded the whole image from the red upwards, probably owing to rapid evaporation from the heat of the spectrum (*b*). Exterior bleaching frequently took place in the course of the ex-



periments, permanent in some instances, while in others it vanished as the surface dried. When water was used with the juice instead of alcohol, the general character of the image was similar to that described, except that the small figure beyond the violet was more distinct, and seemed to bear the same proportion to that formed by the rest of the spectrum which the length of the lavender rays bears to the length of the sum of the others. The bleached part round the whole was more extended, and a faint crimson haze encompassed the dark spots, which were very distinct (*c*).

(358.) "The following are some of the cases in which the simultaneous effect was produced. For example, paper washed with the juice of the petals of *Globe Amaranthus* in distilled water, on exposure to the spectrum, acquired a delicate pink tint which was soon bleached to whiteness from the upper edge of the green to the end of the lavender rays, while at the same time a perfectly circular spot of equal whiteness was seen under the red rays and a little way below them, which had the appearance of being an image of the sun. After more washing with the juice, the two bleached parts were united by a long white neck, which speedily vanished, and was succeeded by a dark crimson image, whose greatest intensity of colour was under the yellow rays. At some distance below the red rays two crimson spots were strongly marked, especially the uppermost, both surrounded by a paler halo.



(359.) "The juice of the petals of pale blue *Plumbago auriculata*, in distilled water imparted its tint to writing paper, which after exposure to the action of diffused Light acquired a pale yellowish green hue. The part under the lavender and violet rays of the spectrum, repeatedly washed with the juice, assumed a pale brown colour. The indigo rays seemed to have no effect, although, from their lowest edge to the distance of half the length of the spectrum below the red rays, a lavender

blue image was formed. Under the orange rays a minute indigo-coloured spot appeared, and also a larger spot of the same colour under the yellow, which were soon blended into one, forming a single oblong figure of maximum intensity, surrounded by a halo of paler indigo. An isolated disk of the same colour as the halo, with two dark spots in its centre, appeared at some distance below the red rays.

(360.) "The juice of the *Beet-root*, in a strong solution of common salt, imparted a pink colour to the paper, and the most refrangible rays acquired a powerful bleaching energy; the pink ground was whitened under the lavender, indigo, and blue; a deep crimson spot was formed under the yellow, with a rose-coloured halo, elongated to the bleached part on one side, and to the end of the orange on the other, while a hazy rose-coloured disc was visible at a distance below the red. The crystallisation of the salt on this figure was, in proportion to the intensity of colour, most on the crimson spot and its halo, and on the coloured disk, but scarcely any on the bleached portion."

(361.) The great number of instances now adduced, in which we have distinct evidence of *chemical change* under the influence of the sun's rays appear sufficient to support the position I have long maintained, that the solar rays are continually acting upon matter—it signifies little in what form it may be presented to its influence. Although for photographic purposes we can only select those compounds which exist in a state of "tottering equilibrium," at least, in the present state of our knowledge, yet we have distinct evidence, that a sunbeam cannot fall upon any solid body without leaving permanent traces of its action.

## CHAPTER VI.

## THE INFLUENCE OF THE SOLAR RAYS UPON VITAL ORGANISATION.

(362.) THE surface of our earth is rendered beautiful by the almost countless forms of vegetable life which adorn it. On the bare surface of the wind-beaten rock, the mysterious lichen finds a sufficient amount of those elements which assimilate and form its structure, to support it through all the stages of its growth; and at length, having lived its season, it perishes, and in its decay forms a soil for plants, which stand a little higher in the scale of vegetable life. These again have their periods of growth, of maturity, and of dissolution; and by their disintegration, form a soil for others, which pass through the same changes, until at length the once naked rock is covered with a garden, and the flowering shrub and the enduring tree wave in loveliness above it.

(363.) In a short time we find the almost microscopic seed, placed in a few grains of earth, springing into life, developing its branches, unfolding its leaves, and producing flowers and fruit. Although it has become a stately plant, we shall not discover much diminution of the soil from which it grew, and from which it would, at first, appear it derived all those solid matters of which its structure is composed. Experiments have been made in the most satisfactory manner, and it has been proved, that a very small amount only, of the soluble constituents of a soil are taken up by the roots of a plant; we have then to look to other sources for the origin of the woody matter, of the acid and saccharine juices, of the gums and of the resins, yielded by the vegetable world. These are all, it will be found, formed by some mysterious modifications of

a few elementary bodies. The plant in virtue of its vitality, and under the excitement of the solar rays, effects the assimilation of these elements; and these are the phenomena which it is the business of this section to examine.

(364.) The conditions necessary to germination are moisture, a moderate temperature, and the presence of oxygen gas. The experiments of Ray, Boyle, Scheele, Achard, and Humboldt, all show that the presence of atmospheric air is necessary. Germination cannot take place at the freezing point of water, and at  $212^{\circ}$  all vitality is destroyed. If seeds are kept quite dry, they will not germinate, although the other conditions are fulfilled. All seeds do not germinate at the same seasons, some requiring a more elevated temperature than others, which fact explains the cause of the different periods at which we find the plants springing from the soil.

It has already been remarked, that Michellotti proved Light to be injurious to germination, and Ingenhouz and Sennebier found that seeds germinated more rapidly even beneath the soil in the shade than in sunshine. This fact has been now established beyond all doubt.

(365.) Priestley's Experiments\* on the influence of growing plants upon the air are most instructive; and since they are not generally known, it is thought advisable to give an abstract of them in this place. "Without *Light*," says Priestley, "it is well known that no plant can thrive; and if it do grow at all in the dark, it is always white, and is, in all other respects, in a weak and sickly state. Healthy plants are probably in a state similar to *sleep* in the absence of Light, and do not resume their proper functions but by the influence of Light, and especially the action of the rays of the sun."

Again, arguing that the green matter which forms in water grows and gives off gas by the influence of Light

\* Experiments and Observations relating to various Branches of Natural Philosophy, with a continuation of the Observations on Air. By Joseph Priestley, LL.D., F.R.S. Birmingham, 1781. Vol. II.



alone, Priestley gives the following experiment: "Having a large trough of water, full of recent green matter, giving air very copiously, so that all the surface of it was covered with froth, and jars filled with it, and inverted, collected great quantities of it, and very fast; I filled a jar with it, and, inverting it in a basin of the same, I placed it in a dark room. From that instant no more air was yielded by it, and in a few days it had a very offensive smell, the green vegetable matter with which it abounded being then all dead and putrid." Dr. Priestley then instituted a series of experiments to prove that the *green matter*, and not the water, produced the air. Rumford imagined that any porous body, as cotton, wool, silk, and even threads of glass, would separate air from the water: Priestley's experiments were singularly conclusive on this point.

(366.) Priestley continued his experiments with the higher order of plants:—"Having by this means fully satisfied myself that the pure air I had procured was not from the *water*, but from the green vegetating substance assisted by Light, I concluded that other *aquatic plants* must have the same effect; and going to a piece of stagnant water, the bottom of which was covered with such plants, I took five or six different kinds promiscuously. Then having put them into separate jars of the water in which they were growing, and inverted them in basins of the same, I placed them in the sun, *and I found that all of them, without exception, were immediately covered with bubbles of air*, which, gradually detaching themselves from the leaves and stalks where they had originated, rose to the surface of the water; and this air, being examined, appeared to be, in all the cases, very pure, though not quite so pure as that which was before procured from the green matter."

(367.) It must be remembered that Carbonic acid was unknown to Priestley and those who laboured in the same field with him. Dr. Ingenhousz\*, for example, says, "The

\* Ingenhousz's Experiments on Vegetables.

air obtained from the leaves is by no means air from the water, but air continuing to be produced by a *special operation carried on in a living leaf* exposed to the daylight, and forming bubbles, because the surrounding water prevents this air from being diffused through the atmosphere.

\* \* \* \* It is wonderful that this green matter seems never to be exhausted of yielding dephlogisticated air, though it has no free communication with the common atmosphere, from which the most part of other plants seem to derive their stock of air. Does this vegetable matter imbibe this air from the water, and change it into dephlogisticated air? This does not seem to me probable. I should rather incline to believe that the wonderful power of nature, of changing one substance into another, and of promoting perpetually the transmutation of substances, which we may observe everywhere, is carried on in this green vegetable matter in a more ample and conspicuous way."

(368.) Dr. Priestley, with his usual ingenuity, very soon determined that the plants separated some gas from the water, which they decomposed, and that, after a time, they ceased to give out air in water. He says, "I put a handful of these water plants, without distinguishing their kinds, into a receiver containing eighty ounce measures of water, inverted in a basin of the same; and when they had yielded between six and seven ounce measures of air, I examined it, and found that, with two equal quantities of nitrous air, the measures of the test were 0.8. But *the air had been diminishing about three days*, so that I believe there had been eight ounce measures in all, or one-tenth the capacity of the jar, and certainly purer than it was now found to be. It was evident, therefore, that *no more air would have been produced by these plants in water, though placed in the sun.* \* \* \* \* It is also a proof that the proper origin of all the air produced in these circumstances is not the plant and the Light, and that these are only agents to produce that effect on something else; that

in all cases, the quantity of air produced bears a certain general proportion to the capacity of the vessel in which the process is made." Again, "I have found a slower and a less produce of air from rain water than from pump water; owing, I suppose, to the rain water containing less air to operate upon, and generally also in a purer state, than that which is contained in pump water." We now know that the latter contains more carbonic acid than the former.

(369.) These experiments were continued by Priestley with cabbage leaves, lettuce, the spurge, cucumber, potatoes, white lilies, and many other kinds of plants: in all of them proving the decomposition of fixed air (carbonic acid) by the *living* vegetable matter in the water under the influence of Light. We find philosophers, both at home and abroad, repeating Dr. Priestley's experiments, and gradually arriving at a correct interpretation of the observed phenomena. Cavendish, in his experiments on air, wanders round the truth, but is continually drawn away from it by the hypothesis of Phlogiston. Sennebier found that plants yielded more dephlogisticated air (oxygen) in distilled water impregnated with fixed air than in plain distilled water. On this, Cavendish says, "For as fixed air is a principal constituent part of vegetable substances, it is reasonable to suppose that the work of vegetation will go on better in water containing this substance than in other water."

M. Monge, in his memoir "Sur le Résultat de l'Inflammation du Gaz Inflammable et de l'Air Déphlogistique dans des Vaisseaux Clos," also examines this question. About this time the complete explanation afforded by Lavoisier's annihilation of the Phlogistic Hypothesis, led to correct explanations of the facts; and we advance more steady in our inquiries.

(370.) My investigations on this subject were first published in the Philosophical Magazine for April, 1840, and they have, since that time, been continued with little interruption. The progress of the inquiry was recorded in

the Reports of the Association for several years. It is necessary for a correct understanding of the results obtained, that all the conditions under which the experiments have been made should be distinctly stated.

(371.) Six boxes were so prepared, that air was freely admitted to the plants within them, without permitting the passage of any of the solar rays, except those which passed through the coloured media with which they were covered.

These media permitted the permeation of the rays of Light in the following order :—

1. A RUBY GLASS, *coloured with Oxide of Gold*. — This glass permits the permeation of the ordinary red, and the extreme red rays only.

2. A BROWN-RED GLASS. — The extreme red ray appeared shortened ; the ordinary red ray and the orange ray passed freely, above which the spectrum was sharply cut off.

3. ORANGE GLASS. — The spectrum was shortened by the cutting off of the violet, indigo, and a considerable portion of the blue rays. The green ray was nearly absorbed in the yellow, which was considerably elongated. The whole of the least refrangible portion of the spectrum permeated this glass freely.

4. YELLOW GLASS, *somewhat Opalescent*. — This glass shortened the spectrum by cutting off the extreme red ray, and the whole of the most refrangible rays beyond the blue ray.

5. COBALT BLUE GLASS. — The spectrum obtained under this glass was perfect from the extreme limits of the most refrangible rays down to the yellow, which was wanting. The green ray was diminished, forming merely a well-defined line between the blue and the yellow rays. The orange and red rays were partially interrupted.

6. DEEP-GREEN GLASS. — The spectrum is cut off below the orange and above the blue rays. Although the space on which the most luminous portion of the spectrum falls, appeared as large as when it was not subjected to the ab-

sorptive influence of the glass, there was a great deficiency of Light, and on close examination with a powerful lens, a dark line was seen to occupy the space usually marked by the green ray.

(372.) A case was also prepared, containing five flat vessels filled with different-coloured fluids.

A. RED. *Solution of Carmine in Supersulphate of Ammonia.* — This gives a spectrum nearly in all respects similar to that given by the ruby glass (1.); all the rays above a line drawn through the centre of the space occupied by the orange being cut off.

B. YELLOW. *A saturated Solution of Bichromate of Potash.* — This beautifully transparent solution admits the permeation of the red and yellow rays, which are extended over the space occupied by the orange ray in the unabsorbed spectrum. The green rays are scarcely evident.

From the absorptive powers of the sulphurets of lime and potash in solution, I was very desirous of using them, but they were found to be so liable to decomposition when exposed to the sun's rays as to be quite useless for my purposes: sulphuretted hydrogen being liberated in such quantities as to burst the bottles with great violence.

C. GREEN. *Muriate of Iron and Copper.* — This medium is remarkably transparent; the blue, green, yellow, and orange rays pass freely, all the others being absorbed.

D. BLUE. *Cupro-sulphate of Ammonia.* — This fluid obliterates all the rays below the green ray, those above it permeating it freely.

E. WHITE. — This is merely water rendered acid by nitric acid, for the purpose of securing its continued transparency. It should be noted that spaces in the boxes have been left open to the full influence of the Light, that a fair comparison might be made between those plants growing under ordinary circumstances, and the others under the dissevered rays.

(373.) It will be seen from the above, that the following combinations of rays have been obtained to operate with.

1. and A. The calorific rays well-insulated.
  2. A smaller portion of these rays mixed with a small amount of those having peculiar illuminating powers.
  3. The central portion of the solar spectrum well-defined, and all the rays of least refrangibility, thus combining the luminous and calorific rays.
  4. The luminous rays mixed with a small portion of those having a calorific influence.
  5. The most refrangible rays with a considerable portion of the least so; thus combining the two extremes of chemical action, and affording a good example of the influence of the calorific blended with the chemical spectrum.
  6. Some portion of those rays having much illuminating power, with those in which the chemical influence is the weakest under ordinary circumstances.
- B. The luminous rays in a tolerably unmixed state.
- C. The luminous rays combined with the least actively chemical ones, as in 6.; but in this case the luminous rays exert their whole influence.
- D. The most refrangible or chemical rays well-insulated.

E. White Light.

(374.) From these arrangements it will be evident, that, although we do not secure the complete isolation of the rays, as we should do with a prism, we obtain the great preponderance of one influence over others, which suffices to insure, to a certain extent, the decided action of that one. I am well aware that we only arrive at approximations to the truth by the system adopted, but I am unacquainted with any method by which these experiments could be continued for any time, otherwise than with absorptive media.

(375.) When we look on a spectrum which has been subjected to the influence of some absorptive medium, we must not conclude, from the coloured rays which we see, that we have cut off all other influences than those

which are supposed to belong to those particular colours. Although a blue glass or fluid may appear to absorb all the rays except the most refrangible ones, which have usually been considered as the least calorific of the solar rays; yet it is certain that some principle has permeated the glass or fluid, which has a very decided thermic influence, and so with regard to media of other colours.

The relative temperatures indicated by good thermometers placed behind the glasses and fluid cells, which I have used, will place this in a clear light. The following results present a fair average series, and distinctly mark the relative degrees in which these media are permeable by the heating rays:—

## GLASSES.

Colour.	Luminous rays not absorbed.	Temperature.
1. Ruby.	Ordinary red, and the extreme red -	- 87°
2. Red.	Ordinary red, and orange, portion of extreme red	83°
3. Orange.	Little blue, green, yellow, orange, red, and extreme red - - - -	- 104°
4. Yellow.	Red, orange, green, and blue - -	- 88°
5. Blue.	Violet, indigo, blue, little green, and some red -	- 84°
6. Green.	Orange, yellow, green, and blue -	- 74°

## FLUIDS.

A. Red.	Ordinary and extreme red - -	- 78°
B. Yellow.	Ordinary red, and yellow - -	- 80°
C. Green.	Blue, green, yellow, orange - -	- 69°
D. Blue.	Green, blue, indigo, violet, and trace of red -	- 73°
E. White.	All the rays - - - -	- 89°

In these examinations the highest temperature was not obtained behind the red media, but behind those which have a yellow or orange tint.

Such were the arrangements adopted: these were sometimes slightly varied, but not to an important extent. The results obtained will be best understood by my report to the British Association in 1847, which I reprint with but little alteration.

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*Researches on the Influence of the Solar Rays on the Growth of Plants.*

(376.) The experiments connected with this investigation have been extended over a period of seven years; they have been made at every season of the year; and the localities in which they have been carried on has been changed from the south-western extremity of the kingdom to the neighbourhood of the metropolis.

Although there are many important points which remain open for investigation, and others, which although examined, require, from the complexity of their phenomena, still more minute research, I believe I am enabled to lay before this meeting of the British Association a series of important facts connected with the processes of germination and vegetable growth, as affected by solar radiations.

The title heading to each of my former reports has been the "Influence of Light," &c. I have now changed that form of expression and adopted the above. My reasons for this are, that much confusion has arisen from our habit of referring all the effects observed in the processes of vegetation to the agency of Light, whereas it appears that some agencies which are not *luminous* materially influence the phenomena of vegetable vitality.

Without entering into any discussion in this place on the probable existence, or otherwise, of a principle distinct from Light and Heat in the sun's rays, to which we refer the curious chemical changes produced by solar influence, it will be sufficient to admit the existence of three distinct classes of phenomena, which cannot, I think, be disputed.

These are luminous influence, LIGHT; — calorific power, HEAT; — and chemical excitation, ACTINISM.

The problem which these researches were directed to solve was the proportion and kind of influence exerted by



Light, Heat, and Actinism—as the principle supposed to be active in producing the chemical phenomena of the solar rays has been called—in the various stages of vegetable growth.

(377.) The means we have of separating these phenomena from each other are not very perfect; indeed, in the present state of our knowledge, it is impossible to have evidence of the operations of either Light, Heat, or Actinism absolutely separated from each other. If we use the prismatic spectrum, we have over every portion of it a mixture of effects. Even in the mean yellow, or most luminous ray, we have a considerable amount of thermic action, and, under some circumstances, evidence of chemical power. In the violet rays, which have been particularly distinguished as chemical rays, we have light and heat; and in the calorific rays we have decided proof of both luminous and actinic power. In the experiments which have been made with the prismatic spectrum, we have in fact no certainty that the results stated to be due to a particular ray—that ray being regarded as the representative of a particular phenomenon—are not the combined effect of the three forces.

The same objections apply to absorbent media, but the amount of each influence is readily determined; and we are therefore enabled to refer any particular result to a tolerably well-defined agency.

(378.) All the experiments recorded in this report have been made under the action of those radiations which have permeated variously coloured media, such as tinted glass and coloured transparent fluids. It is not sufficient to state that a yellow, red, or blue glass or fluid was employed, as it by no means follows that these media are permeated only by the rays corresponding in colour, or by the influences due to a given order of refrangibility.

The difficulties which oppose themselves to experiments made with coloured media have been strongly felt by other observers. Dr. Daubeny says, in his memoir “On

the Action of Light upon Plants," &c., Philosophical Transactions, vol. cxxvii. 1836, "The difficulty, however, of comparing the relative intensity of the light transmitted by the variously coloured media, which were employed in my experiments, induced me to content myself with showing that the effect of Light upon plants corresponds with its illuminating, rather than with its chemical or calorific influence; and to waive the more difficult inquiry, whether its operation upon the vegetable kingdom exactly keeps pace with the increase of its own intensity."

(379.) In my previous reports to the British Association in 1842 and 1844, I have stated the kind of examination to which I then subjected each coloured screen. Many effects which have from time to time presented themselves, have convinced me of the necessity of a still more close examination of the order in which radiant principles permeate the media employed. I have therefore in every case examined with all care the illuminating, calorific and chemical effects of the solar rays which have passed the media employed.

The amount of Light has been determined by measuring off, in parts of an inch, the prismatic rays which pass the screen. This is preferable to any system of measuring which depends upon the power of the eye to appreciate either light or shadow. Having formed a well-defined spectrum on a white tablet, and carefully marked off the centre of the yellow ray as being the point of maximum Light, and the limits of each of the other rays, the transparent coloured medium was interposed, and the amount of absorption observed. These examinations, many times repeated, were made with reference to the luminous rays only; and in the description of my experiments, I shall, considering the unabsorbed ray as being represented by 100, express the amount of light actually effective by such a number as may give the sum of the rays measured off after permeation.

The calorific influences which escape absorption, and

which have been determined by the expansion of the mercury in a thermometer with a blackened bulb placed behind the coloured glass or fluid, and by the evaporation of ether from a sheet of blackened paper, as recommended by Sir John Herschel, will be expressed numerically in the same way as light, without reference to the colour of any ray. I am far from considering the thermic influences of the solar rays as quite independent of the colour of the ray with which they may be associated; but in these experiments on plants, it appears to me, we can only deal satisfactorily with the total amount of radiant heat which is active under the conditions of the experiment, the terrestrial heat being in all comparative experiments the same.

It has indeed been shown by Dr. James Stark (Philosophical Transactions, vol. cxxiv. 1833.), by direct experiment, and indirectly by other observers, that colour exerts a very powerful influence on the conduction, radiation, and permeation of heat.

(380.) The determination of the chemical principle of the solar rays, or actinism, permeating the media employed, required more exact attention than the other phenomena. Dr. Daubeny ascertained this by placing paper washed with nitrate of silver behind the coloured screen; and in my early experiments I was satisfied with using tolerably sensitive chloridated photographic papers for the same purpose.

The experience of many years enables me now to state that we are not acquainted with any transparent medium which is absolutely opaque to actinism. Although nitrate of silver, or indeed any of the salts of silver remain unchanged behind yellow glasses and fluids, yet chlorophyll is deoxidized and turned yellow by the chemical principle which is enabled to permeate them. Upon all those bodies on which *Light* exerts a direct and determinate influence, as upon the organized compounds (particularly the sensitive photographic preparations now employed — 1854),

we find that the changes due to *actinic* power are but slightly interfered with, whereas upon all those inorganic bodies which undergo a change when exposed to the solar chemical radiations, that change being entirely due to actinism, Light acts as a powerfully interfering agent. The conditions under which these antagonistic forces — Light and Actinism — operate upon each other are unknown to us; but it is certain that every combination of an inorganic salt with an organic body presents a different scale of action.

(381.) Nitrate of silver uncombined with organic matter undergoes no change by the influence of any portion of the solar spectrum, or of white light; spread it on paper, or combine it with gum or gelatine, and all that portion of the spectrum above the green ray blackens it; and if we combine this salt with unstable organic compounds, the blackening is found to take place, eventually, under every spectral ray. The other salts of silver, and metallic salts in general, are affected in precisely the same manner. From a knowledge of these facts it became evident that some means must be devised for ascertaining, as correctly as possible, the entire quantity of this chemical principle passing any particular media, without which knowledge any result would be almost valueless. In every instance I have therefore determined the influence of the modified radiations: first, upon the most sensitive silver salts; secondly, upon organic bodies, as the coloured juices of leaves and flowers, and on chlorophyl; and thirdly, upon combinations of the organic and inorganic materials. In this way I have arrived at a degree of correctness which has not been hitherto reached, and the results of the experiments have consequently a higher value.

(382.) I have repeatedly stated that seeds would not germinate under the influence of Light deprived of that principle on which chemical change depends. This statement has been objected to by Dr. Gardner (American Journal of Science, Jan. 1844, vol. xlv.), on the results of

some experiments tried by him in 1840 in Virginia with the prismatic rays themselves. It, however, unfortunately happens that we are not furnished with any knowledge of the degree of stability which he was enabled to ensure for the prismatic rays with his heliostat. Dr. Gardner's researches corroborating those of Dr. Draper are, without doubt, valuable; but for the reasons which I have already given, I must contend that we do not secure a separate action of Light and Actinism by the prism so effectually as by the use of absorbent media. I shall have to mention a modification of my views as to the production of chlorophyl; but I am still convinced, after the experience of many years, that Light is injurious to germination, and that Dr. Gardner's experiments must have been deceptive. Indeed I cannot do better than quote the remarks of Mr. R. Harkness (*Phil. Mag.* vol. xxv. N. S. p. 340., 1844) in reply to Dr. Gardner on this point: — "We know, both from the observations of Ingenhousz and Sennebier, as well as from daily experience, that the absence of solar Light is one of the conditions almost necessary for the germination of seed, and consequently we should not expect that ray in which the maximum of Light is found to facilitate germination, but on the contrary, as in Mr. Hunt's experiments, to retard it.

"This, however, is not the only objection to which this statement is liable, for if the yellow ray be the operating cause by which carbonic acid is decomposed (as stated by Dr. Gardner) and chlorophyl produced, we should also expect that, so far from assisting in germination, it would exercise a highly injurious influence. We know that the presence of oxygen is necessary for the vegetation of seeds, and also that this oxygen is absorbed, and by uniting with a portion of the carbon of the seed reappears in the form of carbonic acid, a process the opposite of that which takes place when chlorophyl is produced. This change is required in order that the amylaceous principle in the seed may be rendered sufficiently soluble for the

support of the germ, previous to its being able to obtain the requisite nutriment from the soil; so that, if the decomposition of carbonic acid be owing to the yellow ray, this same ray ought to be the last to produce any effect on the germination of seeds."

As it is, however, possible that some source of error may exist in my experiments, I shall distinctly state every form of apparatus employed by me, and the actual conditions of the solar radiations under which the different results were obtained.

(383.) In the first place I shall record my experiments on germination.

It became important to determine if any effect was produced by white Light. For the purpose of ascertaining this a quantity of common cress (*Lepidium sativum*) and turnip-seed (*Brassica napus*) was placed upon moist earth and very lightly covered with fine sand; one half was screened from the Light by a blackened board, and the other freely exposed. Under the shaded half the germination was between two and three days in advance of the exposed portion.

This experiment was repeated, using a glass trough containing a weak solution of bichromate of potash half an inch in thickness over the illuminated portion. This solution admitted the permeation of 87 parts of the luminous rays, 92 of the calorific rays, and 27 of the chemical rays. The object in this instance was to ascertain if any greater retardation was produced by the luminous rays, from which the chemical principle was to a considerable extent removed, than by pure white Light, which it will be borne in mind I propose to regard as a compound of 100 parts of each, Light, Heat, and Actinism. The result was that the seed under the influence of this yellow medium did not germinate until five days after the seeds in the dark part of the box.

Upon substituting a solution of sulphate of chromium and potash which admitted the permeation of 85 parts of

Light, 92 parts of Heat, and only 7 of Actinism, the germination was prevented entirely in four experiments; and in the fifth, ten days after the seeds in the dark had germinated, half a dozen of seeds of cress showed symptoms of germination. These experiments were many times repeated and always with similar results. We have thus satisfactory evidence that Light deprived of the principle or power of chemical action arrests the development of the plant, by preventing the vitality of the germ from manifesting itself.

Although the visible sign of germination is the process of chemical combination of the carbon with oxygen and hydrogen, yet the power influencing this change is of an occult character, though evidently dependent on some external excitation, which I have proved not to be Light, or the principle producing the phenomena of colour. We may now, without fear of being misunderstood, declare as a law that in its relation to vegetable life *LIGHT prevents germination*.

(384.) It now became important to ascertain if the chemical principle of the solar rays produced any acceleration of the germinative process. With this view, a box was prepared, in which was placed moist flannel, and this was kept wet by an under layer of water. One half could be completely screened from the Light, and the other half exposed to any influence which it was thought desirable to try.

The luminous rays were obstructed by the interposition of a series of blue glasses, and by solutions of sulphate of copper, or ammoniate of copper.

The tested glass admitted the permeation of—Light 40, Heat 72, and of Actinism 90 parts.

The trough of sulphate of copper obstructed more Heat but admitted the passage of a larger quantity of Light. It gave on examination, Light 60, Heat 54, and Actinism 93 parts.

The solution of ammoniate of copper was of so deep a

colour that only 25 parts of Light passed it, and 48 of Heat, whilst from 93 to 95 of Actinism escaped any absorption.

Common cress (*Lepidium sativum*), Mignonette (*Reseda odorata*), Ten-week Stocks (*Mathiola incana*), and Minor Convolvulus, were placed on the moist flannel, and the tested glass frame being placed over the undarkened half, the box was exposed to sunshine in a warm room. The cress under the actinic influence exhibited signs of germination within twenty-four hours, but no change was observable beyond a swelling of the seed from the absorption of water over that portion in darkness: on the second day all the cress had germinated over the exposed parts, and the other seeds were apparently in a forward condition; whereas in the dark, with the exception of the cress in which germination was established, but little alteration was seen in the other seeds. Although the periods of germination differed in each variety of these seeds, under the conditions to which they were exposed, yet in every instance the seeds influenced by actinic radiations germinated in one half the time which those seeds placed in the dark required.

The experiment was repeated, the seeds being placed *in* earth instead of *on* moist flannel. In every experiment the seed germinated in much less time under the influence of the actinic rays than in the dark.

Several arrangements were made for the purpose of ascertaining if the influence of the chemical rays was confined to the surface of the soil, or if they extended below it. The result was, that I obtained the most satisfactory evidence, that under the influence of the rays which passed the blue glasses, germination was set up at a depth below the surface, at which under the ordinary conditions it did not take place. The common cress, placed an inch below a somewhat clayey soil, germinated with difficulty under the ordinary conditions, but the influence of the actinic radiations was such that germination was but slightly retarded. Various other seeds were tried, particularly



Groundsel	-	-	Senecio vulgaris.
Convolvulus	-	-	Convolvulus minor.
Vetches	-	-	Vicia sativa.
Oats	-	-	Avena sativa.
Ten-week Stocks	-	-	Mathiola annua.
Mignonette	-	-	Reseda odorata.

In every instance germination was set up by the agency of the radiations, which had permeated the blue glasses in a less time, and at a greater depth in the soil, than in comparative experiments in which the seed was exposed to the full influence of Light and its associated radiations as combined in the ordinary solar beam.

When a solution of sulphate of copper was employed, admitting, as we have seen, more Light than the glasses, the evidences of the acceleration of germination were not so great. These experiments were, however, very satisfactory, as being enabled to regulate with considerable nicety the relative proportions of Light and Actinism, they afforded the means of ascertaining the retarding influence of the luminous power. After a great number of experiments, it became evident, that as the relative quantity of the luminous principle was increased, so was the influence of the chemical radiations diminished. In using the ammoniate of copper, as stated, the germination of all the seeds tried became more rapid; and that this was not the mere influence of shading was evident from the fact, that germination under the influence of the deepest coloured solution of the ammoniate of copper, provided it was transparent, was always more rapid than in the dark.

It is evident therefore, that this first spring of vitality is due to some power or principle of solar origin, which is very broadly distinguished from the luminous or colour-giving principle. The manner in which this power is exerted on seed beneath the soil is not clear to us; we know not if it is a mere disturbance of something already diffused through matter, or an emanation from the sun: all we are enabled to declare is, that *the germination of*

*seed is more rapid under the influence of the actinic rays, separated from the luminous ones, than it is under the influence of the combined radiations or in the dark.\**

(385.) Sennebier (*Physiologie Végétale*, tome troisième, 398.), although not acquainted with the properties of the chemical principle as separated from Light, has, in reply to some objections of Bertholon (*Journal de Physique*, 1789), who attributed the differences observed between the influences of Light and Darkness on germination to the varying rates of evaporation under the dissimilar conditions, related some experiments on the germination of peas, beans, &c., "placés sur des éponges également humides enfermées sous de petits récipients semblables et d'une égale capacité," which are conclusive; and in a following paragraph he places the question in its true view, as far as the luminous rays are concerned in the phenomena:—

"Il paraît donc que la lumière retarde la germination, et c'est pour prévenir ce retardement, que les graines semées doivent être couvertes de terre," &c. Ingenhousz (*Expériences sur la Végétation*, vol. ii.) has shown that seed deposited in the darkness of the soil germinates sooner than in the light.

These facts my experiments go to establish; and in addition they prove that there exists an influence which is always associated with Light, which has the property of accelerating the process by which the embryo swells, bursts through its integuments, sends its radicle into the soil, and shoots its cotyledons upwards towards the Light.

The conditions of the seed in this process are tolerably well understood. The seed, a highly carbonized body, is placed in a position by which its starch ( $C_{12}H_{10}O_{10}$ ) is changed into gum ( $C_{12}H_{11}O_{11}$ ) and sugar ( $C_{12}H_{14}O_{14}$ ). Here we have a large absorption of oxygen; and experiment has shown that carbonic acid ( $CO_2$ ) is formed. The

\* Messrs. Lawson and Sons, of Edinburgh, have confirmed this result in practice on a large scale.—See Letter published in the Author's "Poetry of Science," 3rd edition, and Appendix.

whole process is the same in character as the blackening of a solution of nitrate of silver, holding organic matter, in the sunshine. Without the organic body the silver salt remains unchanged; with it a combination with the oxidised carbon is effected at the same time as the organic particles take the oxygen from the oxide of silver in solution. All this is known to be entirely dependent on actinic power, and independent of luminous action, and the whole process of conversion in the seed is of a like character. The cotyledons being formed and the plumula exposed above the soil, the conditions are entirely changed, and new influences become necessary to ensure vigorous vegetation.

(386.) If the young plant continues to grow under the influence of the rays which have permeated the blue media employed, it will for some time grow with great rapidity, producing, however, succulent stalks which soon perish. Even in the earliest stages of growth it will be found, that the plants grown in the full sunshine, or under the influences of yellow or red media, representing the luminous and calorific principles, give a larger quantity of woody fibre and less water than those grown under actinic influence. Comparative experiments were several times made for the purpose of testing this point.

Plants growing in the shade in like manner contain more water than those growing in full sunshine, hence we cannot infer that anything more than the deprivation of Light influences the condition of the plants in these experiments. I have ascertained that quite as great a difference exists in the water found in plants growing in artificial shade, and plants of the same class growing unsheltered, under the ordinary conditions of sunshine. It is therefore evident that all these experiments which have been made on the increase of grass crops by littering the fields with boughs of trees and the like, are liable to the error alluded to; and it is very questionable if the increased product of an acre is not principally due to water,

rather than to any carbonaceous product, consequently the increase of the nutritive property is not in the ration of the increase of weight.

(387.) Coloured solutions were employed, and their results compared with similar plants grown under a glass trough filled with very clear water. The plants cultivated were the cress, ten-week stocks, and Venus's looking-glass. An equal weight of the plants was taken from each compartment, and thoroughly dried at the temperature of boiling water with great care. The following table exhibits the results :—

	White Medium.		Red Medium.		Yellow Medium.		Blue Medium.	
	Per cent.		Per cent.		Per cent.		Per cent.	
Admitting of Luminous rays	97		56		90		51	
" " Heat do.	75		84		82		60	
" " Actinic do.	93		29		20		94	
Plants grown.	Wood. grs.	Water. grs.	Wood. grs.	Water. grs.	Wood. grs.	Water. grs.	Wood. grs.	Water. grs.
Cress ( <i>Lepidium sativum</i> ).								
1st Experiment . .	8.2	91.8	8.0	92.0	8.1	91.9	7.2	92.8
2nd Experiment . .	8.1	91.9	8.2	91.8	8.3	91.7	7.0	93.0
3rd Experiment . .	8.4	91.6	7.9	92.1	8.4	91.6	7.6	93.4
Ten-week stocks ( <i>Matthiola incana</i> ).								
1st Experiment . .	22.0	78.0	21.5	78.5	22.2	77.8	20.4	79.6
2nd Experiment . .	22.7	77.3	21.7	78.3	23.0	77.0	21.0	79.0
3rd Experiment . .	21.9	78.1	21.4	78.6	22.5	77.5	19.6	80.4
Venus's looking glass ( <i>Campanula speculum</i> ).								
1st Experiment . .	12.1	87.9	11.7	88.3	12.0	88.0	10.4	89.6
2nd Experiment . .	12.6	87.4	11.9	88.1	12.0	88.0	11.0	89.0
3rd Experiment . .	12.5	87.5	12.0	88.0	12.3	87.7	10.5	89.5

(388.) By continuing, however, the experiment for a longer time under the influences already described, we learn that the actinic radiations exert a power on the plant, which, although I have previously described it, I shall particularly call attention to in this place.

It frequently happens, when the media employed cut off a large quantity of Light and admit the actinic principle

freely, that no formation of leaves takes place after the development of the plumule or first leaf-bud ; the young stem instead of solidifying remains soft, and, without increasing in diameter, continues to elongate until at last it attains to an enormous length. Nothing like this occurs under the influence of either Light or Heat. It would appear that this abnormal condition is due to the excitement of the actinic rays, acting possibly with great power upon the living principle in the roots, by which the elaboration of some organisable matter is produced, which they supply as food to the stem ; but, as there is but little power to decompose carbonic acid, there is not the necessary supply of carbon to give rise to those stems and leaves which naturally form upon the primitive stock.

(389.) That this is something like a true explanation is further proved by the fact, that in the practice of planting shoots the use of blue media is highly advantageous. It appears to increase the tendency to the development of roots, and it is satisfactory to learn that some gardeners have, without any knowledge of the cause, employed cobalt blue glasses to aid in the "striking of cuttings." Dr. Lindley (*Theory of Horticulture*, p. 215.), referring to the experiments of Dr. Daubeny, seems disposed to regard the effects described as due to the absence of Light merely ; it is, however, evident that the chemical principle of the solar beam materially assists in the development of new roots from cuttings. The formation of woody fibre depending on the secretion of carbon from the carbonic acid absorbed by the leaves, and decomposed, by some functional power of the plant, under the influence of external excitement, it has ever been considered important to determine if this was due to the luminous rays or to any others.

(390.) The experiments of Sennebier (*Mem. de Phys. Chim.* tom. ii. p. 55.) went to prove that plants decomposed the carbonic acid they absorbed by the leaves much more readily under the influence of the violet rays than any

others; and in my early experiments I thought I had proved the correctness of Sennebier's position. Dr. Daubeny in England and Dr. Gardner in America have repeated the experiments, and they both conclude from their results that the decomposition of the carbonic acid increases with the increase of Light, and that it is more rapid under the influence of the yellow ray than any other. The natural inference from the experiments which I have already described, in which it is shown that the larger quantity of woody matter is found in those plants which have had the largest amount of Light, is, that *Light is essential to the formation of woody fibre.*

Numerous experiments have been made by placing the leaves of plants in water containing carbonic acid, and then subjecting them to the influence of the modified radiations after permeation of coloured media. Although the quantity of carbonic acid decomposed, or of oxygen liberated by the plant is very different, for the same plant, under different conditions of radiation, it is evident that under any circumstances where Light is admitted, the decomposition of the carbonic acid is effected in some cases slowly, in some with rapidity.

This power of decomposing carbonic acid under the influence of the solar rays is a function due to some vital principle; for I have again and again proved the correctness of Matteucci's statement (*Supplement à la Bibliothèque Universelle de Genève*), that "toute espèce de feuille qui a été coupée et broyée ne donne plus de trace d'oxygène quand on l'expose au soleil dans de l'eau imprégnée d'acid carbonique." Further than this, I have found that more oxygen is given off from a growing plant than from a branch broken from the plant; and that still less is given off from the leaves cut from the branch than when they are attached to it.

(391.) Different plants not only decompose carbonic acid in different rates, but they exhibit greater or less sensibility to luminous influence. This will be apparent from

the following results. The coloured media used were the same as those described. The relative proportions of mixed gas evolved is given, the proportions of nitrogen and oxygen not being ascertained, as the object was merely to test the general sensibility to luminous influence. Each set of the experiments, similarly numbered, were made at the same time, and all the conditions alike except the analysing media. The comparison is made with the result of full exposure to bright sunshine, the gas thus collected being considered as 100.

	Yellow.	Red.	Blue.
<b>Mentha viridis.</b>			
1	64	50	47
2	70	56	51
3	68	56	52
4	71	55	49
<b>Brassica oleracea.</b>			
1	79	66	37
2	81	71	44
3	73	60	42
<b>Mathiola incana.</b>			
1	63	60	58
2	62	59	55
3	67	63	60
<b>Salvia officinalis.</b>			
1	59	51	48
2	62	58	52
3	57	51	46
4	60	56	50

It will be seen from these results that the common cabbage-leaves give more gas under the influence of the luminous rays than the others, but much less under the influence of the actinic principle, combined as it is with 51 per cent. of Light. On the contrary, the ten-week stocks and the sage give less gas than either the cabbage or the mint under luminous influence; but relatively a

much greater proportion under the influence of the chemical and luminous rays combined.

I have, from numerous experiments which I have made, every reason to believe that it will be found that there is as great a difference between the effects produced on growing plants by the prismatic rays, as we know to be the case on photographic preparations; the maximum effect altering, perhaps, for every variety of plant.

(392.) The conclusions I am induced to draw from these experiments are, that the luminous principle of the sun's rays is essential to enable the plants to effect the decomposition of the carbonic acid of the atmosphere and form their woody structure; that some plants require more Light than others to effect this decomposition; as, for instance, we find the sage and ten-week stocks decomposing carbonic acid with less Light than the cabbage or the mint; and it would appear that the increase of the luminous excitement beyond a certain point does not produce a corresponding increase in the quantity of gas liberated from the leaves of these plants. We may infer from all the results obtained and described in this and former reports, that the decomposition of the carbonic acid by plants under the agency of Light is not a simple chemical operation, as has been supposed by some, effected by the chlorophyl, but the result of an exertion of the vital principle of the growing plant, which requires the external stimulus of Light to call it into action.

(393.) A great number of comparative experiments have been made with the unabsorbed prismatic rays, with a view to the settlement of a point on which an American philosopher and myself are at issue, this gentleman having published results the very opposite to those which I have obtained and published. The method pursued has been to place leaves in small tubes filled with water impregnated with carbonic acid, and to place these tubes across the rays formed by a very excellent flint-glass prism. The results have varied with every experiment. If we place a small



sprig covered with leaves in the tube, we get the largest quantity of gas in one ray; if we remove the leaves from the branch, we shall then get the most gas under another ray. No two plants, as far as I am aware, give the same quantity of oxygen, in the same time, under the influence of the same ray, and the age of the plant most materially alters all the effects; the same plant at one age giving evidence of being excited most readily by the blue rays, and at another by the yellow or the red rays. Moreover, I am satisfied that by removing a member, whether a branch or a leaf, from the plant, we give a shock to the living system, which prevents our obtaining any result which shall actually represent the true conditions of the growing plant. On this point the experiments of Matteucci (Cimento, Juillet et Août, 1846) are most satisfactory.

In all experiments on plants, it must be borne in mind that we are dealing with an organised body endowed with peculiar vital functions. As these are ever liable to derangement from numerous causes which are almost beyond the reach of our examination, it is only by a great number of experiments that we can arrive at an approximation to the truth. As I have pointed out, anything which at all interferes with the functional powers of the growing plant, materially alters all the conditions which we are desirous of examining; hence I am perfectly satisfied that all the experiments made with leaves in tubes of water exposed to the prismatic rays are fallacious, and do not at all represent the powers of the plant to which the leaves belong. It is, however, evident, from a careful comparison of the results obtained, that *Light* as distinguished from *heat* and *actinism*, is the principle on which the secretion of carbon and the evolution of oxygen by plants depend.

(394.) Decandolle succeeded in producing the green colour of leaves by the strong Light of lamps, which we know give out a much larger quantity of yellow rays than any others; consequently it was inferred that Light was

necessary to the production of chlorophyl. Dr. Daubeny, however, obtained no result from the action of incandescent lime, which emits a much purer white Light, producing also chemical effects in a marked manner.

Dr. Lindley refers the formation of the colouring matter of leaves to the "effect of decomposing carbonic acid and exhaling oxygen" by the agency of Light, the intensity of colour being in general "in proportion to the decomposing cause, that is to say, to Light." This view is adopted also by Macquart, from whom indeed Dr. Lindley takes it (*Theory of Horticulture*, p. 86.). More recently Dr. Gardner has published a memoir "On the Action of Yellow Light in producing the Green Colour of Plants," &c. (*the American Journal of Science*, vol. xlv. January 1844), in which he contends that he has settled the question beyond dispute, that the yellow rays produce chlorophyl in leaves. It is evident from the statement of results as given by this observer, that the greening was not even in his experiments confined to the yellow ray, but was produced by the orange, green and blue rays, and, as I infer, by the mean red. These experiments were made with great care, and the arrangements of the heliostat, prism and lens appear to have been as complete as possible. I must, however, be allowed to express a doubt if the rays could be kept stationary upon any line for so long a period as six and a half hours, and the slightest movement would vitiate the experiment and render it hazardous to declare that "the centre of the yellow ray is the point of maximum effect in the production of chlorophyl."

(395.) My experiments, made in the same manner as Dr. Gardner's, do not give the same results. The method in which I proceeded was as follows:—A heliostat placed outside a window directed a pencil of light upon a flint-glass equilateral prism, and the prismatic spectrum was received in the dark chamber of an ordinary photographic camera; the place of the lens being occupied by a diaphragm which admitted the passage of the spectral image

only. My apparatus would not allow of my keeping the spectrum upon the same lines for more than three hours, even when in the best adjustment. I found that over every part of the spectrum giving Light and colour recognisable by the unaided eye, the leaves of seedlings of the common cress, mustard, mignonette and peas, which were in an etiolated state, became, after a longer or shorter time, green. In these, as in the experiments previously named, I found that every variety of plant employed appeared to be influenced by different rays. Cress and mustard became green the most rapidly in the green ray, mignonette in the yellow, and peas in the blue. It must be, however, observed that the influence was always most decided between the limits of the mean orange and the mean blue ray, and that it took much longer to green plants in the red than it did in the blue ray.

(396.) Such are the results I have obtained with the spectrum ; and notwithstanding that objections have been urged against the use of coloured media in experiments of this class, I am, after many years' experience, convinced that there is no other way of obtaining correct results. All the colours of the spectrum are merely modifications of the intensity of luminous power, and it has been shown that Light, heat and chemical action, or actinism, are common to every ray, the difference being only proportional. Therefore, because an effect is produced in the yellow ray, we have no evidence that Light alone is the agent ; it may be due to the combined influence of Light and the other principles. We have the means of analysing with great correctness the permeability of coloured media, and we can with considerable facility, by increasing the colour or thickness of a fluid medium, produce almost any order of radiation, which may be maintained for days or months in a constant character. A yellow medium does not imply the use of a yellow Light, or a red one the passage of red rays only ; but a well-regulated yellow medium will give the most Light with the least quantity of actinism, and a

blue one the largest amount of actinism with the least quantity of Light. It will now be understood that I place more confidence in the results obtained under coloured media than any which can be obtained with the prismatic spectrum upon growing plants.

(397.) We have seen that Light is required for the secretion of carbon and the liberation of oxygen; we know that the green colour of plants depends upon solar agency; but unless we can suppose Light to be at one and the same time decomposing carbonic acid, and composing carbon oxygen and hydrogen in the form of the waxy matter chlorophyl, which is not according to the usual order of natural phenomena, we must look for information beyond that afforded us by the experiments named. Indeed, under a solution of bichromate of potash, I have had plants growing, which were very deficient of greenness. This has several times occurred under a glass which cut off seventy-five per cent. of actinism, and admitted ninety-five per cent. of Light. Again, behind a cobalt blue glass admitting eighty of actinism and not more than twenty per cent. of Light, plants have been quite as much etiolated. It is clear, therefore, that the formation of chlorophyl is not directly dependent upon either Light or actinism regarded as isolated principles.

(398.) In the greater number of my experiments with the prismatic spectrum, the greening of the plant has commenced over the space occupied by the green rays; and, under green glasses, which admitted all the rays above the orange ray, plants have invariably grown of a very green colour. The influence of the solar rays upon the green colouring matter of leaves removed by infusion and pressure, extends with tolerable uniformity over every ray of the spectrum, from the red to the violet (Sir John Herschel, "On the Action of the Rays of the Solar Spectrum on Vegetable Colours," *Phil. Trans.*, vol. cxxxiii.). In this case the green colour is, however, destroyed, and a ruddy brown of the same character as the brown of the

leaf in autumn is produced. This change appears to be due to Light and Heat rather than actinism, and presents a curious contrast to the results on inorganic compounds. Here we appear to have a deoxidation of the chlorophyl produced by Light— a process analogous to the decomposition of carbonic acid by the living plant. It is difficult, however, to apply experiments made with dead vegetable matter to such as possesses the principle of life. I am led to infer from the facts, that plants will grow of a pale green colour under the influence of strong light (as admitted through yellow glass), and also under the radiations which permeate deep blue glass (actinic), whilst the heat radiations which pass glass coloured with oxide of gold, and very lightly smoked glass, have a constant tendency to produce a certain degree of ruddy brownness, even in healthy green plants; and that chlorophyl is not formed by the agency of either of those principles alone, but that it results from the combined influence of Light and Actinism, In every experiment made with media which cut off the heat rays, but which admit the luminous and actinic rays, the plants grow of a lively green; and the extracted green of their leaves is preserved without change much longer than under any other conditions. To produce chlorophyl, a recombination of the elements which Light assists the plant to separate from the water and the air is necessary; and I have little doubt but long-continued and carefully conducted experiments will prove that chlorophyl results from the combined influences of Light and actinism in exciting one of those mysterious functions of plants which excite the admiration, but elude the curiosity, of every vegetable physiologist.

(399.) I have previously stated that I have rarely succeeded in getting plants to flower under the influence of any of the media which cut off those rays usually termed the calorific rays. For instance, under intense yellow, deep blue, or very dark green glasses, however carefully the plants may have been attended to, there was seldom any

evidence of the exertion of their reproductive functions. This evidently arises from the necessity of some check upon the chemical actions which depend on Light and actinism, and which exhaust the elements in the formation of wood and vegetable juices which are necessary for the production of those principles which go to the preservation of the species. By removing plants when in a healthy condition from the influences of isolated Light or actinism to a situation where they may be exposed to the effects of those heat radiations which are of the least refrangible class, flowers and seed are rapidly produced.

This is not an effect of heat (*quoad heat*), since the same temperature may be maintained under all the circumstances, yet if the red rays are obstructed, flowers will not form. It is therefore evident that this very remarkable property must depend upon some function peculiar to this class of rays. The researches of Sir John Herschel, Dr. Draper, M. Claudet, and myself on the action of the rays of the spectrum on photographic preparations, must materially assist us in explaining this phenomenon.

Sir John Herschel (Philosophical Transactions, vol. cxxxi. 1840) has shown that the red rays in some cases exalt the oxidation of a silver salt; that they exert a protective power, and even prevent the darkening of paper covered with chloride of silver under the influence of diffused Light (Report of the British Association, 1839).

In the Philosophical Magazine, vol. xvi. N.S. pp. 272-3, I have described several experiments, which prove not merely the protecting power of this red ray, but a power of producing the closer combination of the chemical elements of a compound exposed to its influence. More recently Dr. Draper (Philosophical Magazine, 1846) and M. Claudet, who communicated his experiments to the Meeting of the British Association at Oxford, an abstract of which appears in the present volume, have shown that this class of rays does not merely protect the chemical compound from any change, but that after the sun's rays

have produced a change, they have the power of again restoring the compound to its original condition.

(400.) All these experiments have been repeated with many modifications, and particularly the influence of this class of rays on growing and dead vegetable matter has been particularly observed.

Leaves inspire carbonic acid and give out oxygen. It has been shown by Priestley, Scheele, and Ingenhousz, that flowers consume much more oxygen than any other part of the growing plant. Saussure has shown that flowers will not be developed without oxygen; that, so far from giving out oxygen when exposed to sunshine in larger quantities, as leaves do, they consume even more oxygen than before. Here we find the process which has brought the plant to this stage of growth is reversed, and in place of the decomposition which is effected by Light and actinism, we have a process of reoxidation or of a close assimilation of elements, precisely analogous to that which we detect upon the Daguerreotype plate and on photographic papers under the influence of the red rays.

The results to which my experiments have led me, are —

- 1st. Light prevents the germination of seeds.
- 2nd. Actinism quickens germination.
- 3rd. Light acts to effect the decomposition of carbonic acid by the growing plant.
- 4th. Actinism and Light are essential to the formation of the colouring matter of leaves.
- 5th. Light and actinism, independent of the calorific rays, prevent the development of the reproductive organs of plants.
- 6th. The heat radiations corresponding with the extreme red rays of the spectrum facilitate the flowering of plants and the perfecting of their reproductive principles.

(401.) I have been led to detect some very remarkable differences in the composition of the solar rays by frequently examining the condition of the solar radiations,

according to the plan described at the commencement of this Report, for the purpose of ascertaining as nearly as possible the exact conditions in which the luminous, actinic, and calorific principles exist. During the year 1846 and the commencement of 1847, being engaged in selecting a glass for the glazing of the great Palm House in the Royal Botanic Gardens at Kew, this examination has been more exact and continuous.

It should be stated that the object was to obtain a glass which should prevent the scorching solar rays from injuring the plants. The result has been in every way as satisfactory as could be desired — no case of scorching having been detected during the five years since the completion of the Palm House.\*

In the spring I find the actinic principle the most active, and, as compared with Light and heat, in very considerable excess.

As the summer advances, the quantity of Light and heat increases relatively to the actinic principle, in a very great degree.

In the autumn, Light and actinism both diminish, and the calorific radiations are, relatively to them, by far the most extensive.

It should be again explained, that by *Light* I mean to express all those rays of the spectrum which are visible to a perfectly-formed human eye; by *actinic principle*, the principle to which the phenomenon of chemical change under solar influence belongs; and by *calorific radiations*, not merely those effects which are traceable by any thermometric instruments, but also those which we can detect by the protection from change, produced by a class of rays existing near the point of maximum heat in the spectrum.

In the spring, when seeds germinate and young vegetation awakes from the repose of winter, we find an excess of that principle which imparts the required stimulus; in the summer, this exciting agent is counterbalanced by

\* See Appendix.



another possessing different powers, upon the exercise of which the structural formation of the plant depends; and in the autumnal season these are checked by a mysterious agency, which we can scarcely recognise as heat, although connected with thermic manifestations, upon which appears to depend the development of the flower and the perfection of the seed.

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(402.) A few remarkable results must yet be noticed. Under all ordinary circumstances plants bend in a very decided manner *towards the Light*. In all my experiments with red fluid media *they have as decidedly bent from it*. I do not know how to explain this as the effect of mere heat; it would appear that some property resides in the red rays which acts in opposition to the general law. Further investigations are required on this point.

(403.) The soil in which the plants grew was the same in all the boxes used, but it was several times observed that, under the yellow glasses and fluids, fungi made their appearance. From the occurrence of these vegetables under the same circumstances on several occasions, I was naturally led to observe their production with greater care. I could not, with the utmost attention, make the *Agaricus muscarius* grow behind any other absorbent media than the yellow, under which it grew luxuriantly. This appears, in some measure, to explain the popular notion, that mushrooms, and plants of that variety, grow most abundantly under the influence of bright moonlight. It has been found that the heat of the rays of the moon is very limited, and the amount of chemical action which has been detected is exceedingly small; we must therefore regard the moonbeams as consisting largely of the luminous rays, the other active rays being in all probability absorbed by the moon's surface.

(404.) The changes which take place in the seed during

the process of germination have been investigated by Saussure: oxygen gas is consumed, carbonic acid is evolved; and the volume of the latter is exactly equal to the volume of the former. The grain weighs less after germination than it did before; the loss of weight varying from one third to one fifth. This loss of course depends on the combination of its carbon with the oxygen absorbed, which is evolved as carbonic acid. According to Proust, malted and unmalted barley differs in the following respects:—

			Unmalted.			Malted.
Resin	-	-	1	-	-	1
Gum	-	-	4	-	-	15
Sugar	-	-	5	-	-	15
Gluten	-	-	3	-	-	1
Starch	-	-	32	-	-	56
Hordein	-	-	55	-	-	12

This shows that the insoluble principle hordein is, in the process of germination, converted into the soluble and nutritive principles starch, gum, and sugar. We are therefore at present left in considerable doubt; we can only suppose that the luminous solar rays act, as indeed we find them to do on many of the argentine preparations, in preventing those chemical changes which depend upon the absorption of oxygen. A like interference has been observed by Sir John Herschel to be exerted by the extreme red rays of the spectrum; and, from the manner in which germination is impeded in the seeds covered by a deep red media, we may trace a somewhat similar influence.

(405.) The woody fibre of plants, and all the carbon which is found as an elementary constituent of the resins, gums, juices, &c., of the vegetable world, is derived exclusively from the atmosphere, to which it is supplied by the respiration of animals, and all those processes of combustion which are continually going on.

By some peculiar function, the leaves of plants during

every moment of their lives are absorbing carbonic acid. It has been stated that the reverse of this takes place during the hours of darkness, and that at night the leaves absorb oxygen, and exhale carbonic acid. It appears to me that this statement has been made without sufficient consideration, or the requisite experimental evidence. "This reversal at night," says a most talented philosopher, "of what was done in the day, may, at first sight, appear at variance with the unity of plan which we should expect to find preserved in the vegetable economy; but a more attentive examination of the process will show that the whole is in perfect harmony, and that these contrary processes are both of them necessary in order to produce the result intended." He then, evidently feeling the difficulty of the question, proceeds to explain this harmony as follows. "The water which is absorbed by the roots generally carries with it a certain quantity of soluble animal or vegetable materials, which contain carbon. This carbon is transmitted to the leaves, where, during the night, it is made to combine with the oxygen they absorb. It is thus converted into carbonic acid, which, when daylight prevails, is decomposed; the oxygen being dissipated, and the carbon retained. It is evident that the object of the whole process is to obtain carbon in that precise state of disintegration, to which it is reduced at the moment of its separation from carbonic acid, by the action of solar light on the green substance of the leaves; for it is in this state alone that it is available in promoting the nourishment of plants, and not in the crude condition in which it exists when it is pumped up from the earth, along with the water which conveys it into the interior of the plant. Hence the necessity of its having to undergo this double operation of first combining with oxygen, and then being precipitated from its combination in the manner above described." These passages are selected, not with any view of reflecting upon their accomplished author, but because they afford the best expression

of the views which have been generally entertained on the strength of the experiments of Saussure and Grischow, which admit of another explanation.

(406.) It is the green parts of plants, principally the leaves, and to a less extent the bark, which absorb carbonic acid. Plants grow in soils composed of divers materials and they derive from these, by the soluble powers of water which is taken up by the roots, and by mechanical forces carried over every part, carbonic acid, carbonates, and *organic matters containing carbon* (?). Evaporation is continually going on, and water escapes freely from the leaves during the night, when the functions of the vegetable, like those of the animal world, are at rest. "A cotton wick," says another experimental philosopher, "inclosed in a lamp which contains a liquid saturated with carbonic acid, acts exactly in the same manner as a living plant in the night. Water and carbonic acid are sucked up by capillary attraction, and both evaporate from the exterior part of the wick."

(407.) A plant placed in a vessel containing water impregnated with carbonic acid, and carefully closed, so that no water could escape by evaporation except through the plant, was placed under the receiver of an air-pump in which was put some pure potash, and a good exhaustion effected. The potash was found to have absorbed carbonic acid. The same arrangement was made, only that the water now used was *distilled*. Under the same circumstances in every respect, a like quantity of moisture was found to be absorbed by the caustic potash, but of course no carbonic acid. In these experiments the carbonic acid and water were mechanically drawn through the plant.

Precisely similar arrangements were placed under bell glasses filled with atmospheric air, which was dried and freed from carbonic acid, by exposure to potash for some time. In neither case could any diminution of the quantity of oxygen be detected, but traces of carbonic acid

were found in the air in which the plant in the carbonated water was placed. These experiments were made in the dark, and eudiometric examinations of the air have convinced me that some oxygen gas is always given off.

There is no reversion of the processes which are necessary to support the life of a plant; the same functions are operating in the same way by day and by night, but differing greatly in degree. During the hours of sunshine, the whole of the carbonic acid absorbed by the leaves, or taken up with water by the roots, is decomposed, all the functions of the plant are excited, the processes of inhalation and of exhalation are quickened, and the plant pours out to the atmosphere streams of pure oxygen, at the same time as it removes a large quantity of deleterious carbonic acid from it. In the shade, the exciting power being lessened, these operations are slower, and in the dark they are very nearly, but certainly not quite, suspended.

(408.) We have now certain knowledge. We know that all the carbon which forms the masses of the magnificent trees of the forests, and of the herbs of the fields, has been supplied from the atmosphere, to which it has been given by the functions of animal life, and the necessities of animal existence. Man and the whole of the animal kingdom require, and take from the atmosphere, its oxygen for their support. It is this which maintains the spark of life, and the product of this combustion is carbonic acid, which is thrown off as the waste material, and which deteriorates the air. The vegetable kingdom, however, drinks this noxious air; it appropriates one of the elements of this gas—carbon—and the other—oxygen—is liberated again to perform its services to the animal world. It is not possible to conceive a more perfect, a more beautiful system of harmonious arrangement than this, making the animal and the vegetable kingdoms mutually dependent. The existence of the one ceases when the other is destroyed. If the vegetable world was

swept away, animal life would soon become extinct; and if all animal existence was brought to a close, the forest would fall, and the flowers of the field, which now clothe the earth with gladness, perish in the utterness of a lamentable decay. It has been supposed that the vegetable world was called into existence long previous to the creation of animals, and to this period is referred the formation of the coal strata. There might have been an epoch when the disturbed condition of the earth—its earthquake shocks, and volcanic strugglings, may have poured so large a quantity of carbonic acid into the atmosphere, as to have rendered this planet unfit for the habitation of animals, until a teeming and most gigantic vegetation, by exhausting it for their own supply, purified the air, and rendered the more quiet earth a fitting abode for creatures endowed with reason and with instinct. But the hypothesis is unsupported by facts, and it is not within the range of probabilities that the animal or vegetable kingdoms can ever have an independent existence.

(409.) The animal kingdom is constantly producing carbonic acid, water in the state of vapour, nitrogen, and, in combination with hydrogen, ammonia. The vegetable kingdom continually consumes ammonia, nitrogen, water, and carbonic acid. The one is constantly pouring into the air what the other is as constantly drawing from it, and thus is the equilibrium of the elements maintained.

Plants may be regarded as compounds of carbon vapour, oxygen, hydrogen, and nitrogen gases, consolidated by the all-powerful, all-pervading influences of the solar ray; and all these elements are the produce of the living animal, the conditions of whose existence is also greatly under the influence of those beams, which are poured in unceasing flow from the centre of our system. Can any thing more completely display a system of the loftiest design, and most perfect order, than these phenomena?

(410.) The most casual observer could not fail to remark the peculiar influences of the solar agencies, at

different seasons of the year. In spring, a fresh and lively green pervades the field and forest; this in summer assumes a darker hue, and in the autumn passes gradually into a russet brown. In a very early stage of my photographic researches, I discovered a remarkable difference in the chemical action exerted by the solar rays an hour or two before noon, or an hour or two after it. I was convinced at an early period, and the continued observations of many years prove, that similar differences are to be detected between the solar emanations of the vernal and the autumnal periods. The change in the colour of the leaves appears to be entirely dependent upon the absorption of oxygen, which all the green parts of plants have the power of absorbing, almost without intermission. This true case of chemical affinity, it would appear, goes on equally with the spring or the summer leaves; but during these periods the vital force, under the stimulus of the Light, is exerted in producing the assimilation of the oxygen for the formation of the volatile oils, the resins, and the acids. In the autumn this exciting power is weakened; the summer sun has brought the plant to a certain state, and it has no longer the vital energy necessary for continuing these processes. Consequently, the oxygen now acts in the same manner on the living plant, as we find in experiment it acts upon the dried green leaves, when moistened and exposed to its action. They absorb gas and change colour.

Sir John Herschel observes, in reference to the action of Light on the juices of plants: "The earlier flowers of any given species reared in the open air, are more sensitive than those produced, even from the same plant, at a late period in its flowering, and have their colours more completely discharged by Light. As the end of the flowering period comes on, not only the destruction of the colour by Light is slower, but residual tints are left which resist obstinately." These residual tints are the same which produce the brown of the autumnal leaf;

and the same agent may be traced in the production of photographs upon papers spread with expressed juices, and on the changing colours of flowers and of leaves.

(411.) A remarkable example of the influence of Light upon the juice of plants, is the *Cacalia ficoides*, cited by Liebig. During the hours of darkness, this plant, like others, assimilates oxygen, and in the morning it is as acid to the taste as the sorrel. By the influence of the morning sun it loses this oxygen, and at noon it is tasteless; and by the continued action of the Light still more is abstracted, and the plant is positively bitter in the evening.

(412.) Experiments have been instituted with a view of ascertaining if any particular ray of the spectrum had the power of inducing, more powerfully than others, the progress of plants towards the Light, a phenomenon which is strikingly exhibited by the potato. It would appear that the yellow — luminous — rays exert this influence with the greatest force; the blue rays exerting, as might have been expected from their small illuminating power, no influence — and the red rays causing the plant to bend in an opposite direction.



## CHAPTER VII.

THERMOGRAPHY.—A PARTICULAR EXAMINATION OF ALL THE PHENOMENA CONNECTED WITH THE SUPPOSED RADIATION OF LIGHT IN ABSOLUTE DARKNESS.

(413.) NOTHING having been done in this section of the inquiry since this chapter was first published, it stands without alteration.

It may appear to many at first, that this inquiry is not quite in place in the present volume, it having been shown that the conclusions arrived at by M. Moser, who first called particular attention to the phenomena in question, are in all probability erroneous. The subject is, however, so intimately united with those agencies whose powers we have been considering, that this treatise would be incomplete, did it not contain a particular account of the discovery, the discussion to which it has given rise, and record all those experiments of interest which bear upon these mysterious actions.

(414.) In a memoir "On Vision and the Action of Light on all Bodies,"\* M. Ludwig Moser first announced the following fact: "*If a surface has been touched in any particular parts by any body, it acquires the property of precipitating all vapours which adhere to it, or which combine chemically with it on these spots, differently to what it does on the other untouched parts.*"

In a memoir entitled "*Some Remarks on Invisible Light*,"† and in another "*On the Power which Light possesses of becoming latent*,"‡ his views were still further

\* Poggendorff's Annalen, vol. lvi. p. 177. No. 6. 1842.

† Poggendorff's Annalen, vol. lvi. p. 569. No. 8. 1842.

‡ Poggendorff's Annalen, vol. lvii. p. 1. No. 9. 1842.

Those papers have been translated by Henry Croft, Esq., and published in Taylor's Scientific Memoirs, vol. iii. part xi. February, 1843: from these translations all my quotations will be made.

developed, and I shall now endeavour to place them in as correct a light as possible.

(415.) In the Daguerreotype process those parts of the iodised silver plate upon which the Light has acted with most power, receive, when the plate is exposed to the vapour of mercury, the largest quantity of that vapour over their surfaces, and the gradations of Light are marked very beautifully by the thickness of these mercurial films. Now if we write with a piece of steatite on a looking-glass, the writing is invisible until we breathe upon it, when it appears distinctly. If we place coins on a plate of glass or metal, and allow them to remain for some few hours in contact, although no change will be visible when they are removed, we may bring out beautiful images of the coins by breathing on the plate, or exposing it to any vapour. Upon these experiments M. Moser has based his hypothesis, *That Light of a peculiar degree of refrangibility is absorbed by all bodies, and that they radiate it again in darkness.*

(416.) We must, however, observe all the phenomena which M. Moser has brought before the scientific world. These effects are produced by writing on glass or metal with any substance whatever. "We may first breathe uniformly over the whole plate, and then write on it, either with blotting-paper, a brush, or any thing else; the characters will become visible whenever the plate is breathed on, and this phenomena lasts for some time. Not only is glass applicable to this purpose, but every other polished body exhibits the same appearances: I have tried it with metals, resins, wood, pasteboard, leather, &c. Even fluids may be used; if we take a clean and still surface of mercury, hold over it a body, and breathe on the other parts, or, what is better, breathe on the whole surface first, and then remove the moisture by any gentle means from particular parts, they will again become visible when breathed on, even after several days, if the mercury remains undisturbed. Moreover, absolute *contact* with the

extraneous body is not necessary, mere juxtaposition producing similar effects. If we hold over a polished body a screen, part of which has been cut out according to pleasure, but without allowing it to touch, and then breathe on the whole, and allow the water to evaporate, we shall find that, on breathing on it again, we shall be enabled to distinguish fully the figure of the excised parts : and still farther, it does not require a polished body, inasmuch as *dull* glass exhibits the same phenomena."

(417.) These phenomena were produced in a great many ways. "An engraved metallic plate was warmed, and then held for about half a minute on a well polished piece of silver foil, or a clean mirror plate. When the plates were cold, they were breathed on, and exhibited the above-mentioned appearances in a much more perfect manner ; for not only were the outlines of the body visible, but also the individual figures, letters, &c., and all with the greatest distinctness." Frequently silver or other metallic plates were made warm, and cold bodies, variously cut stones, figures of horn, pasteboard, cork, coins, &c. allowed to remain on them for some time. The phenomena were all the same." Mercurial vapour was found to act in the same manner as the vapour of water, and the vapour of iodine the same as that of mercury. An iodised silver plate, having some of these bodies placed upon it, "was introduced into the vapours of mercury, and then the perfect image became visible, *that is to say, Daguerre's phenomenon was produced without the intervention of Light, for the experiments succeeded just as well by night as by day.*"

(418.) Moser argues from these experiments, "*that contact is capable of imitating the action of Light,*" and he considers the following experiments to prove this clearly : "A silver plate was iodised during the night, and even without the Light of a candle ; a cut slab of agate, an engraved metallic plate, and a ring of horn, &c. were then laid upon it, and the plate was afterwards introduced into

the vapours of mercury. A good, clear picture of all the figures, of the stones, the letters of the plate, and of the ring, was obtained. A plate which had been treated in the same manner was exposed to day or sunlight, and similar pictures were produced. Other plates of the same kind were placed under coloured glasses—yellow, red, and violet; under the first two only a trace of the image was evident; but under the violet glass it was clearly defined." Upon these experiments, Moser remarks, "*the violet rays continue the action commenced by contact.*" He then proceeds to examine the action of Light upon "simple or difficultly changeable bodies:" the results are certainly exceedingly curious and instructive.

(419.) "A new plate of silver was cleaned and polished as well as possible. A surface with various excised characters was suspended over it without touching, and the whole was exposed to the sun for some hours, and directed towards it; after the plate, which of course did not exhibit the least change, had been allowed to cool, it was held over mercury heated to about 60° Reaum. A clear image of the screen was produced; those parts where the sunlight (which had been very weak) had acted, had caused the deposition of a quantity of mercury." Plates of copper and of glass were treated in the same manner, and with the same results. "If we compare the remarkable fact of the action of Light upon surfaces of silver, with the above-mentioned phenomena produced by contact, we can no longer doubt *that Light acts on all bodies*, modifying them so that they behave differently in condensing the vapours of mercury." Moser then proposes the following general expression of the fact: "*Light acts on all bodies; and its influence may be tested by all vapours that adhere to the surface, or act chemically upon it.*"

(420.) If through one of the excised screens we breathe upon a plate of metal or glass, and then removing the screen, allow the vapour to pass off, and then again breathe upon the plate, the vapour will adhere to those

parts which have been protected, and the portions on which the breath was at first condensed will appear dark. The vapours of mercury act in a similar manner. Hence Moser concludes, "*That the same modification is produced in plates when vapours are condensed, as when Light acts on them*" (419).

(421.) "If an iodised silver plate be allowed to remain too short a time in the camera obscura, it afterwards exhibits no image when exposed to the vapours of mercury; a Light film of mercury is deposited over the whole plate, which is not only the case with this, but with a plate of the pure metal and the blackened iodide of silver. If the plate remain a longer time in the camera obscura, a picture certainly is produced, but in which only the brightest parts are depicted, and, which is here of importance, the light parts are of a white colour, *i. e.* they condense the most mercury. If the plate remains still longer in the camera obscura, a picture with all its details is formed; but the bright parts have lost a portion of their whiteness, and appear grey, *i. e.* they do not condense so much of the mercurial vapour. If it be left still longer, on taking it out no picture at all is to be seen; if now inserted into the mercurial vapours, a negative image is produced, or, in other words, these bright parts do not condense any mercury."

(422.) "If Light acts on iodide of silver" (I still quote from the "Memoir on Vision," &c.) "it imparts to it the power of condensing mercurial vapours in an increasing ratio; but if it acts beyond a certain time, it then diminishes this power, and at length takes it away altogether and this happens before the yellow iodide has changed its colour. The vapours of mercury have been seen to do the same, and if in the last-described phenomenon they produce a negative image, it is only what Light would have done had it been allowed to act still longer. Iodide of silver is found to blacken under the influence of the solar rays, and the vapour of mercury also renders it

black: from this M. Moser contends that the action of Light and of mercurial vapours is identical. Numerous other experiments are given by Moser of a similar character. The same effects were produced upon a great many metals, and with numerous bodies, establishing in the most satisfactory manner the remarkable fact "*That when two bodies are sufficiently approximated, they reciprocally depict each other.*"

(423.) Although attention was drawn to a few of these phenomena by Dr. Draper, about two years previously to the publication of the above-mentioned Memoirs, and were used by him in explanation of the phenomena of the Daguerreotype, yet these notices were exceedingly limited; and the great discovery of the remarkable influences which all bodies exert upon each other is indubitably due to Professor Moser.

(424.) In an Addendum to the Memoir on Vision, which bears the date of June 2., M. Moser first proclaimed his hypothesis, "*that every body must be considered as self-luminous.*" In the paper on Latent Light, he further explains himself in the following words: "I have discovered and described another class of rays of Light, those emitted by every body without exception, because it is self-luminous, — rays whose presence is evidenced, by the fact of two sufficiently approximated bodies impressing their images on each other, although every thing that the retina could denominate Light has been excluded. I call them the *invisible rays of Light*, to distinguish them from Ritter's dark rays at the violet end of the spectrum; I might also call them the most refrangible rays, for it appears that their refrangibility is greater than that of the other rays of the spectrum. As I shall show, they are not present in day, or sunlight, and must not, therefore, be confounded with the above-mentioned dark rays."

(425.) Arguing from these facts, that whenever a body condenses vapours differently over its surface, it must have undergone some change, which is produced by some

invisible radiation, Moser infers that such a defined disposition of vapour upon any body is sufficient evidence of the existence of this "*invisible Light*." He has also, with great diligence, pursued his inquiries with a view to determine the *colours* of this "invisible Light," and particularly to ascertain the colours of the rays emitted by each particular body.

(426.) It is necessary to understand this part of his argument. If a Daguerreotype plate is placed in the camera obscura until an image is formed upon it, and if it then be removed, and exposed to the full rays of the sun, the plate is blackened all over and the drawing obliterated. "This destruction of the images does not depend upon the simultaneous action of the differently coloured rays of which it is composed, because blue and violet Light, and partly the green, are capable of performing the same thing." This is what Moser calls "*the Phenomenon of levelling*." Having obtained images by means of the camera on Daguerreotype plates, Moser placed them "on pure silver, gold, copper, mirror-metal, iodised silver, and porcelain;" they were allowed to remain in contact or juxtaposition for a considerable time in the dark, and all the images were found to be nearly effaced. It is concluded from this, that the "invisible Light" has the power of *levelling* the work done by the solar rays. But finding that the images produced as described, by contact, cannot be obliterated by exposure to Light, he concludes "that *visible rays* are not capable of destroying images produced by those which are *invisible*." Now, as the images produced in the camera are not destroyed by mercurial vapour, as they are by the blue and violet rays, but brought out by it, M. Moser infers that the colour of the *latent Light* of mercurial vapour is not blue or violet. A plate is exposed for a very short time in the camera, and brought to such a state that it may be destroyed by yellow Light, or rather Light which has permeated a yellow glass, and it is found

that mercury produces no image; hence it is inferred that "*the colour of the latent Light of the vapours of mercury is yellow.*" The absurdity of all this will presently be shown. By precisely the same reasoning Moser has *established* the colour of the latent Light of iodine to be either blue or violet, and that the latent Light of water "is certainly not green, yellow, orange, or red, but that it appears to belong to the ordinary prismatic colours, inasmuch as I have never seen it destroy an image produced by the invisible rays."

(427.) We are now in a situation to discuss the merits of the hypotheses of the philosopher of Königsberg. In the first place, I must express my disapprobation of any term involving such a contradiction of ideas as that adopted by M. Moser. It is necessary when we engage in an inquiry that we should have a distinct idea of the matter upon which we are to operate, and by all means avoid anything which may lead to confusion in our minds.

INVISIBLE LIGHT is one of the most injudicious expressions that could be conceived. There are invisible rays — as heat rays, and rays having chemical power; but there cannot exist invisible Light. Even supposing the matter, so to speak, of Light, "a substance distinct from all other, existing in darkness, expanded through all things at all times (in a *latent* or *invisible* state), and rendered visible by being properly *excited*;"\* yet it will only tend to confuse us, if we regard, even according to the above notion, this substance as Light previously to its "being properly excited." Those rays which, acting upon some part of that wonderful organ the eye, enable us to distinguish external nature is LIGHT; but that which does not enable animals to see is not Light.

(428.) We will now proceed to the consideration of this interesting and important question. Upon repeat-

\* Scheme of Scripture Divinity, by Dr. John Taylor, published in 1762.



ing the simple experiments above referred to, of placing a disc upon a metal plate and breathing on it, I find that it is necessary for the production of a good effect, to use dissimilar metals; for instance, a piece of gold or platina, on a plate of copper or of silver, will make a very decided image, whereas copper or silver, on their respective plates, give but a very faint one, and bodies which are bad conductors of heat placed on good conductors, make decidedly the strongest impressions when thus treated.

(429.) This is still more strikingly shown by the following experiments\* :—

I placed upon a well-polished copper plate a sovereign, a shilling, a large silver medal, and a penny. The plate was gently warmed by passing a spirit lamp along its under surface; when cold, the plate was exposed to the vapour of mercury; each piece had made its impression, but those made by the gold and the large medal were most distinct,—not only was the disc marked, but the lettering on each was copied.

A bronze medal was supported upon slips of wood, placed on the copper, one-eighth of an inch above the plate. After mercurialisation, the space the medal covered was well marked, and for a considerable distance around, the mercury was unequally deposited, giving a shaded border to the image; the spaces touched by the wood were thickly covered with the vapour.

The above coins and medals were all placed on the plate, and it was made too hot to be handled, and allowed to cool without their being removed; impressions were made on the plate in the following order of intensity, — gold, silver, bronze, copper. The *mass of the metal* was found to materially influence the result; a large piece of copper making a better image than a small piece of silver.

\* “Thermography, or the Art of Copying Engravings, &c. on Metal Plates,” by the Author. Transactions of the Royal Cornwall Polytechnic Society, 1842. — *Philosophical Magazine*, December, 1842.

When this plate was exposed to vapour, the results were as before. On rubbing off the vapour, it was found that the gold and silver had made permanent impressions on the copper.

The above being repeated with a still greater heat, the image of the copper coin was, as well as the others, most faithfully given, but the gold and silver only, made impressions which could not be rubbed out.

A *silvered* copper plate was now tried with a moderate warmth. Mercurial vapour brought out good images of the gold and copper; the silver had marked the plate, but its image not well defined.

By repeating these experiments it will become very evident to every one, that the relative *calorific* relations, materially influence the result, and this is still more strikingly shown by the following arrangements.

I placed upon a plate of copper, blue, red, and orange coloured glasses, pieces of crown and flint glass, mica, and a square of tracing paper. These were allowed to remain in contact half an hour. The space occupied by the red glass was well marked, that covered by the orange was less distinct, but the blue glass left no impression; the shapes of the flint and crown glass were well made out, and a remarkably strong impression where the crown glass rested on the tracing paper, but the mica had not made any impression.

The last experiment being repeated; after the exposure to mercurial vapour, heat was again applied to dissipate it, but the impressions still remained on the plate, although the vapour was volatilized.

I placed the glasses used above, with a piece of well-smoked glass for half an hour, one-twelfth of an inch *below* a polished plate of copper. The vapour of mercury brought out the image of the smoked glass only.

All these glasses were placed *on* the copper, and slightly warmed. Red and smoked glasses gave, after vaporization, equally distinct images; the orange the next; the others

left but faint marks of their forms : polishing with Tripoli and putty powder would not remove the images of the smoked and red glasses.

An etching was made upon a smoked etching ground on glass, and the *glass* being placed in contact with a copper plate, the image of the glass only could be brought out, showing that no influence was exerted through the glass.

A design cut out in paper, was pressed close to a copper plate by a piece of glass, and then exposed to a gentle heat ; the impression was brought out by the vapour of mercury in beautiful distinctness. On endeavouring to rub off the vapour, it was found that all those parts, which the paper covered, amalgamated with mercury, which was removed from the other parts of the plate ; hence there resulted a perfectly permanent white picture on a polished copper plate.

The last experiment, in particular, proves that a very remarkable molecular change is effected ; and, as it would appear, it is dependent upon the bad conducting powers of the paper.

(430.) It was now desirable to ascertain if the solar rays had anything to do with these phenomena.

The coloured glasses before named were placed on a plate of copper, with a thick piece of charcoal, a copper coin, the mica and the paper, and exposed to fervent sunshine. Mercurial vapour brought up the images in the following order : smoked glass, crown glass, red glass, mica, orange glass, paper, charcoal, the coin, blue glass ; thus distinctly proving that the only rays which had any influence on the metal were the calorific rays. This experiment was repeated on different metals, and with various materials, the plate being exposed to steam, mercury, and iodine : I invariably found that those bodies which absorbed, or permitted the permeation of the most heat, gave the best images. Blue and violet glasses could not be detected as leaving any evidence of action. Spectra

imprinted on photographic papers by rays, which had permeated these glasses, gave evidence of the large quantity of the chemical rays which passed them freely, I therefore considered those as without the power of effecting change on compact simple bodies so readily as heat does.

(431.) In a paper which I published in the "Philosophical Magazine," for October, 1840, I mentioned some instances in which I had copied printed pages and engravings on iodized paper, by mere contact and exposure to the influence of the calorific rays, or to artificial heat. I then, speculating on the probability of our being enabled, by some such process as the one I then named, to copy pictures and the like, proposed the name of THERMOGRAPHY to distinguish it from Photography.

I now tried the effects of a print in close contact with a well-polished copper plate. When exposed to mercury I found that the outline was very faithfully copied on the metal.

A paper ornament was pressed between two plates of glass, and warmed; the impression was brought out with tolerable distinctness on the under and warmest glass, but scarcely traceable on the other.

Rose-leaves were faithfully copied on a piece of tin plate, exposed to the full influence of sunshine; but a much better impression was obtained by a prolonged exposure in the dark.

(432.) With a view of ascertaining the distance from each other at which bodies might be copied, I placed upon a plate of polished copper a thick piece of plate glass, over this a square of metal, and several other things, each being larger than the body beneath. These were all covered by a deal box, which was more than half an inch distant from the plate. Things were left in this position for a night. On exposing to the vapour of mercury, it was found that each article was copied, the bottom of the deal box more

faithfully than any of the others, the grain of the wood being imaged on the plate.

(433.) Having found, by a series of experiments, that a blackened paper made a stronger image than a white one, I very anxiously tried to effect the copying of a printed page or a print. I was partially successful on several metals, but it was not until I used copper plates amalgamated on one surface, and the mercury brought to a very high polish, that I produced any thing of good promise. By carefully preparing the amalgamated surface of the copper, I was at length enabled to copy from paper, line-engravings, wood-cuts, and lithographs, with great accuracy.

The following is the process at present adopted by me, which I consider far from perfect, but which affords us very delicate images :—

A well-polished plate of copper is rubbed over with the nitrate of mercury, and then well washed, to remove any nitrate of copper which may be formed ; when quite dry, a little mercury taken up on soft leather, or linen, is rubbed over it, and the surface worked to a perfect mirror.

(434.) The sheet to be copied is placed smoothly over the mercurial surface, and a sheet or two of soft, clean paper being placed upon it, is pressed into equal contact with the metal by a piece of glass, or flat board ; in this state it is allowed to remain for an hour or two. The time may be considerably shortened by applying a very gentle heat, for a few minutes, to the under surface of the plate. The heat must on no account be so great as to volatilize the mercury. The next process is to place the plate of metal in a closed box, prepared for generating the vapour of mercury. The vapour is to be slowly evolved, and in a few seconds the picture will begin to appear ; the vapour of mercury attacks those parts which correspond to the white parts of the printed page or engraving, and gives a very faithful, but a somewhat indistinct image. The plate is now removed from the mer-

curial box, and placed into one containing iodine, to the vapour of which it is exposed for a short time; it will soon be very evident that the iodine vapour attacks those parts which are free from mercurial vapour, blackening them. Hence there results a perfectly black picture, contrasted with the grey ground formed by the mercurial vapour. The picture being formed by the vapours of mercury and iodine, is of course in the same state as a Daguerreotype picture, and is readily destroyed by rubbing. From the depth to which I find the impression made into the metal, I confidently hope to be enabled to give to these singular and beautiful productions a considerable degree of permanence, so that they may be used by engravers for working on.\*

This is the particular process to which I gave the name of Thermography, which name is not inappropriate to the whole class of phenomena, as if not directly the effect of a disturbance of the latent caloric, they are certainly materially influenced by the action of heat.

(435.) For the purpose of ascertaining what part, if any, the solar emanations acted in the instances above referred to, various methods were devised, some experiments being made with coloured absorbent media, and others with the prismatic spectrum itself.

The coloured media used by me, insulated respectively the following rays:—

1. Red, orange, yellow, and some of the blue.
2. Orange, yellow, green, with a faint trace of the blue, and a small portion of the red.
3. Orange, yellow, green, blue.

\* M. Moser made an attack upon the author of this volume, claiming as his own all the published experiments, particularly the above. The question was, however, very satisfactorily decided in the author's favour, in the *Philosophical Magazine* for November and December of 1841. In "*Lerebour's Photography*," the discovery of this process was, by error, attributed to M. Knorr. Since this was written the varied occupations in which I have been engaged, have entirely prevented my pursuing these investigations.

4. Green, blue, indigo, violet, and invisible chemical rays.
5. All the rays passed. White Light.
6. None of the visible rays.—(A bottle of ink.)

A very highly-polished plate of copper, with the above media in flint-glass bottles laid upon it, was exposed to bright sunshine for one hour. The plate was then placed in a dark box, and exposed to the vapour of mercury. The largest deposit of vapour was found to mark the space on which the most calorific rays acted (Medium, No. 1.); the next in order was that influenced by the blue (No. 4.); and then the others as follows: green (3.), yellow (2.), white (5.), and black (6.). There was less mercury deposited on the spaces which these four bottles covered than over the exposed parts of the plate.

(436.) Precisely the same arrangement *was left in the dark* for five hours, and the plate then exposed to mercurial vapour, which attacked it in the same manner as when it had been subjected to strong sunshine, except that no mercury lodged upon the uncovered parts of the plate. Another copper plate was placed one-eighth of an inch *above* the same bottles of fluids *in the dark*, and allowed to remain in that position for five hours; on exposure to mercury it was found that the action was confined to the red (No. 1.), the blue (No. 4.), and the green (No. 3.); which last could scarcely be detected, so faint was the image formed by the vapour. Here we have distinct evidences of radiations in the dark, intimately connected with the thermic properties of the media used.

(437.) Two copper-plate engravings on thin paper were placed, face down, upon two highly-polished and well-amalgamated plates of copper. One of the plates was covered with window-glass, and the other with a beautiful red glass, stained with the oxide of gold. They were exposed to daylight for four hours, during which period there were but faint gleams of sunshine. On subjecting the plates to the vapour of mercury, it was found that under the influence of the red glass a very capital

impression was made; but no trace of any action could be detected on the plate which had been under the white glass.

(438.) Paper patterns were laid upon plates of polished copper, and upon these large bottles of fluids (the same used in the experiments on the influence of Light on plants (361.)) were placed. Being allowed to remain some hours *in the dark*, it was found that the best image was formed on the plate which had been placed under the bottle containing red fluid, but that very decided impressions were made under the others. Exposed to *strong sunshine* for a short period, half an hour, it was found when the plates were mercurialized, that under the red fluid alone was an image formed.

(439.) By placing bad conductors of heat, as wood, glass, and paper, on metal plates, and lowering their temperatures by placing their under surfaces upon vessels filled with freezing mixtures, it was found that the same effect was produced as when the plates had been warmed,—these experiments clearly proving that the phenomena could be produced by any disturbance of the caloric latent in the bodies used.

(440.) Having adjusted a good Heliostat, so that the sun's image was reflected upon a given spot for some hours, this pencil of Light was decomposed by a prism, and then, being concentrated by a large lens, it was thrown upon a polished plate of copper, which was placed in the focus of the lens, and allowed to act upon the plate for periods which varied from one to three hours. In every case the result was the same. The quantity of diffused Light, which always accompanies a prismatic spectrum, produced its effect upon the whole surface of the plate, and a thin film of mercurial vapour covered it. On the spot upon which the rays of least refrangibility fell, a space exactly coinciding with the maximum heating point of the spectrum, as shown by Sir William Herschel, and also with the great heat spot



in the thermic spectrum of Sir John Herschel, the condensation of the vapour was so exceedingly thick, that it stood a distinct white spot upon the plate. Over the whole space occupied by the visible rays, the quantity of vapour was much less than that which covered the other parts; and it was plainly distinguished from the rest of the plate by well-defined lateral lines of vapour. Here we have distinct evidence of the power of the calorific rays; and it would appear that the whole of the luminous spectrum had a negative power.

(441.) Allowing a condensed prismatic spectrum to traverse a similar copper plate for some time, it was found, after exposure to mercurial vapour, that a line of thickly deposited vapour marked the path of the red and the extreme red rays.

(442.) M. Knorr, in pursuing his investigations, found that these images could be produced without any condensation of vapour on the plates, and simply by the action of heat. The process he employs is to place a copper plate over a spirit lamp; upon this is put the plates which are to receive the impressions, and upon the latter the object to be copied. The whole is then slowly heated to the degree at which a well-polished copper plate begins to change colour, when the lamp is extinguished, and the plates and medals withdrawn. Distinct impressions of the bodies to be copied are always found, and these made to a considerable depth into the surface of the metal.

(443.) From these results, it is rendered quite certain that a very extensive class of these phenomena are producible by the agency of heat. M. Moser himself admits the accelerating power of caloric, but he adopts the gratuitous assumption, that this power is only exerted to disturb the "invisible Light." We have very satisfactory evidence, that all bodies are constantly radiating some peculiar and energetic principle from their surfaces. I have frequently proved the existence of these radiations

from iron heated below redness. Under their influence some of the metallic combinations of loose affinity are decomposed, and many of the organic vegetable bodies undergo a rapid change. It is to this principle, in all probability, that the very curious production of the spectral images in question is, in many cases, due.

(444.) It must, however, be shown, that effects in all respects similar may be produced by other agencies than those of heat.

M. Karsten found that if a glass plate was placed upon a metallic one, and on the glass a medal, which was subjected to discharges of electricity, the glass received a very perfect image of the medal, which could be developed by either mercury or iodine. If several glass plates are placed between the medal and the under metal plate, and discharges passed through them, each piece of glass receives an image, but only on its upper surface. For a more detailed account of these very interesting experiments, the reader is referred to M. Karsten's Memoirs.

(445.) My own results would show, that the electro-negative metals make the most decided images upon electro-positive plates, and *vice versâ*. I have also found that electrical discharges have the remarkable power of restoring impressions which have been long obliterated from the plates by any polishing processes; proving, in a very convincing manner, that the disturbances upon which these phenomena depend, are not confined to the surface of the metals employed, but that a very decided molecular change has been effected for a considerable depth into the mass.

(446.) If we cover a copper plate with water or oil, to the depth of 1-16th of an inch, and support upon bits of glass, a medal, so that its under surface just touches the fluid, a very decided image is made upon the copper plate in a few hours. These images are partly visible by the tarnishing of the plate over every part but that which is covered by the medal. Upon pouring off the

fluid and dry polishing, the image is rendered invisible; but on exposing the plate to vapour, it is again brought out.

Some such experiments as these have been interpreted, by Moser, into a proof of the permeability of water and oil to the "invisible Light."

(447.) We have now seen that *LIGHT, Heat, Machine-Electricity*, and a *Voltaic Current*, all produce that disturbance upon the surfaces, at least of solid bodies, which disposes them to receive vapours upon definite spaces. It will also be found, that any *mechanical* disturbance to which the plates may be subjected, will act in precisely the same manner as the above elements. Is it not then most unphilosophical, and indeed exceedingly absurd, to reason in the way M. Moser has done, and upon such very insufficient evidence as is afforded by the manner in which metal or glass plates condense vapours, to build an hypothesis on the existence of a peculiar modification of Light and Colour, neither of which can be rendered evident to the organ of vision?

(448.) I must not quit this discussion without explaining, that the "levelling" action of Light, alluded to by Moser, is nothing more than a darkening of the whole surface, and the "levelling" which he attributes to the "invisible Light" is nothing more than the effect of chemical action. Those parts of the iodized plate which have been changed by Light are restored to their original state in the dark, by the influence of the iodine, which exists in the under unchanged layers on the plates, and in those parts which have been maintained in shadow. The same kind of changes, which are certainly curious and complicated, take place with those photographic images which are procured by the action of an iodide on a darkened salt of silver. With this explanation, it will be seen at once, that the elaborate reasonings of Moser on the colours of the latent Light of vapours are of no value, being in all respects illogical.

(449.) M. Fizeau's speculations on this subject do not properly belong to this work, but as they show that these images may also be produced by causes which have not yet been considered, and from their interest, I give them a place. They are, however, worthy of a more attentive consideration than I can bestow upon them. In the *Comptes Rendus*, November 7. 1842, in a letter to M. Arago, Fizeau thus sets forth his ideas, and gives the results of his experiments: "Far from thinking we must admit the existence of a new species of radiations, escaping from all bodies, even in complete darkness, and subjected in their emission to laws entirely peculiar, I am convinced that no kind of radiations whatever, are to be had recourse to for the explanation of these phenomena, but that we should rather connect them with the known facts which I shall now mention.

" '1. Most of the bodies upon which we operate have their surface clothed with a slight layer of organic matter, analogous to the fatty bodies, and volatile, or at least susceptible of being carried off by aqueous vapour.

" '2. When vapour is condensed on a polished surface, if the different parts of this surface are unequally soiled by extraneous bodies, even in an exceedingly minute quantity, the condensation is effected in a manner visibly different on the different parts of its surface.'

" When, therefore, we expose a polished and pure surface to the contact of, or at a small distance from, any body whatever, with an unequal surface, it will happen that a part of the volatile organic matter which covers this latter surface will be condensed by the polished surface in the presence of which it is; and as I have supposed the body to present inequalities or projections and hollows, that is to say, its different points to be unequally distant from the polished surface, the result of this will be an unequal transfer of the organic matter on the different points of this surface; at the points corresponding to the projections of the body the polished surface will

have received more, and at the points corresponding to the hollows it will have received less; hence, then, there will result a kind of image, but generally invisible. If a vapour be then condensed on this polished surface, we see that it is then under the conditions which I just now mentioned, and that the condensation will take place in a manner visibly different upon the different points, that is to say, the invisible image will become visible." \* This very simple method of accounting for these phenomena, has been adopted by Professor Grove, on the strength of some experiments which show that these images may be very readily formed by the action of any volatile body; and a very eminent authority states, that he has found "many of the phenomena ascribed to *latent Light*, or to *heat*, are owing to the absorption of matter in the state of vapour or minute particles, passing from the object to the surface of the glass or metal upon which the image of that object is impressed; and by this means we have obtained very fine pictures upon glass which are *positive* when seen by reflection, and *negative* when seen by transmitted Light."

(450.) Many of the phenomena may be produced in the way above stated; but M. Fizeau is mistaken in applying his results in explanation of the whole class. I have proved in the most incontrovertible manner, that these images may be produced, when by processes of boiling and heating every trace of organic matter must be removed from the surface. And when we consider that these impressions are, under certain circumstances, formed to a considerable depth beneath the surface, we must admit that, although this may be one of the causes, yet that is only one amongst many others, and indeed one of the least energetic of the lot. All these facts, however, substantiate my position that LIGHT is not the agent which acts in darkness, consequently, that Moser's

\* Scientific Memoirs, vol. iii. p. 489.

position is untenable. At the same time we must not too hastily dismiss the question, as it is probable that amongst the operations of those diversified powers, we may be enabled to detect the existence of one more important than either, which may enable us to trace out the influence which disposes the molecular structure of bodies, and the relations of matter as displayed in the phenomena of chemical affinity.

## CHAPTER VIII.

## ON PHOSPHORESCENCE.

(451.) WE have thus far been considering Light as an emanation from the sun: how far this view is borne out by the facts discovered remains to be decided. There are circumstances which might lead us to consider Light as an essence independent, and universally diffused, and amongst these the most striking are the phenomena of phosphorescence. It has already been stated that Benvenuto Cellini observed it in gems; and a considerable degree of attention was bestowed upon phosphori by the Honourable Robert Boyle. Many minerals have the property of emitting Light when rubbed or broken, and Sir David Brewster has observed the phenomena in upwards of fifty minerals, when they are exposed to a heat below redness in the dark. From these facts we might argue that this *essence* was capable of existing in an invisible state for any period of time; and that it would, when properly excited, produce the effect of Light.\* The eminent authority just now quoted has stated that the phosphoric Light of minerals has the same properties as the direct Light of the sun. This statement must, however, be received with some consideration, if Sir David Brewster means the undecomposed sun-beam. We have no satisfactory evidence which shows that any heat ever accompanies phosphorescent Light, and we have never discovered that it is capable of producing chemical change. By the prism we detect the same number of colours in a phosphorescent beam as in the sun's rays;

\* Edinburgh Phil. Journal, vol. i.

and this is all, I presume, that this talented philosopher intended to imply.

(452.) Many bodies after exposure to the solar rays give out Light when in the dark: this is particularly the case with some flowers, as the *Nasturtium*; and if the human hand is held in the sunshine for half an hour, it will emit Light for some minutes in the dark. The bodies, however, which exhibit this peculiarity in the most remarkable manner are the Bolognian stone, a sulphuret of barium; and Canton's phosphorus, which is prepared by calcining oyster shells and sulphur together. If these substances are exposed to the solar rays, they acquire the property of shining in the dark so strongly, as to enable the observer to distinguish the printed letters on the white page of a book. There are some other substances which exhibit these phenomena: Homberg's phosphorus—the melted chloride of calcium—Baldwin's phosphorus—melted nitrate of lime—the sulphuret of strontian, &c.

(453.) Some of the elder natural philosophers particularly examined the solar phosphori, especially Beccaria, who stated that the violet ray was the most energetic, and the red ray the least so, in exciting phosphorescence in these bodies.

Dessaigues has remarked that the solar-phosphori emit the same character of rays, whatever may have been the kind of Light to which they were exposed.\* This is not, however, very easily reconciled with M. E. Becquerel's experiments. It has been stated by M. Grotthouss that in some diamonds the most efficacious exciting Light is different from that excited. This observer also noticed that electrical discharges restored the property of phosphorescence in cases where it was destroyed by violent heat.

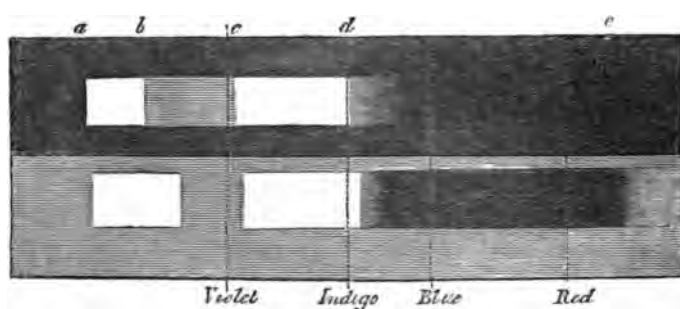
(454.) M. Edmond Becquerel has particularly examined

\* Mem. Inst., tome xi.



the action of the spectrum upon the solar phosphori. The result of his inquiries has been the determination with considerable exactness of the spaces occupied by the rays which impart phosphorescence. He states, that the sulphuret of calcium is rendered phosphorescent by the rays which extend from the indigo to a little beyond the violet; and that two points of maximum intensity are to be detected — one within the visible violet rays, and the other beyond it. The sulphuret of barium exhibits the action of the same rays, but shows only one maximum point, which is situated beyond the violet. Those exciting rays, this observer is inclined to think, have a definite action, and hence he would distinguish them as the “Phosphorogenic rays.” M. E. Becquerel has also observed that the rays below the indigo unto the red, or a little beyond it, have the power of destroying the phosphorescence which the more refrangible rays have excited.

(455.) Many of the experiments of M. E. Becquerel are instructive. Paper being covered with gum Arabic is dusted over with the sulphuret of calcium, and exposed to the action of the spectrum. Upon examining the paper in the dark, two luminous bands are visible, *a*, *b*, *c*, *d*: these spaces correspond with the violet rays, and



the “invisible chemical rays” so called; a dark space exists between these bands, which mark the region occupied by the extreme violet rays, and the lavender rays of Sir John Herschel. If this action is allowed to

continue during a certain time, a quarter of an hour for instance, the diffused Light impresses the remainder of the surface over nearly all parts, so that on examining the paper in the dark, almost the whole surface appears luminous, the parts *a*, *b*, *c*, *d* being the brightest, but the space from the least refrangible indigo to the lowest edge of the red rays is completely dark. The lower part of the preceding wood-cut shows the effect produced. It would appear from this that the rays of less refrangibility than the indigo have the power of preventing phosphorescence, which exactly accords with Beccaria's statement.

(456.) If, before exposing the phosphorescent surface to the action of the spectrum, it is exposed for a few seconds to the solar rays, or diffused Light, it becomes luminous in all its parts. If now we project a spectrum upon it for a few minutes, and then examine it in the dark, it will be found that every part remains luminous except the part *d*, *e*, which has become dark. If the temperature of the surface is raised by a spirit lamp, all the parts previously luminous become vividly phosphorescent, whilst this part remains completely dark.

(457.) By the aid of coloured glass-screens, this is rendered very evident. If a piece of paper prepared with sulphuret of calcium is exposed to daylight, it becomes luminous. By placing immediately on the surface a card which partially covers it, and then a red glass permeable only to the red and orange-coloured luminous rays, and the chemical rays which accompany them, and exposing this arrangement to the sun for a minute, it will be found, on examining the paper in the dark, that the part which has been acted upon by these rays has entirely lost its phosphorescence, whilst every other part is still luminous. The same effect takes place if sulphuret of barium (Bologna phosphorus) is used.

(458.) These experiments distinctly prove that the obscure rays of the spectrum produce phosphorescent

Light, which Light is destroyed by the most luminous and the calorific rays ; a fact which was previously noticed by Seebeck.\*

(459.) M. Biot and the elder Becquerel have proved that the slightest electrical disturbance is sufficient to produce these phosphorescent effects. May we not, therefore, regard the action of the most refrangible rays as analogous to that of the electric disturbance? May not electricity itself be but a development of this mysterious solar emanation?

(460.) A great many animals in the living state emit Light of the character which we have been considering: — the *pholas*, the *medusa phosphorea*, and many other *molluscæ*; the *lampyris* or glow-worm, the *fulgora*, the *scholopendra electrica*, the *cancer fulgens*, and a variety of the *annelids* found in the bogs of Ireland, may be adduced as examples. Nearly all fish in a state of decomposition emit this kind of Light; and the flesh of most quadrupeds in the progress of putrefaction. Rotten wood, it is well known, also evolves a considerable quantity of Light in the dark. The dependence, or otherwise, of these phenomena upon solar influence, remains to be proved. In the Philosophical Transactions for 1790, Dr. Hulme published a very excellent Treatise on Phosphorescence, to which I must refer those who are desirous of obtaining further information on this part of the subject. I cannot refrain from suggesting the importance of experiments to determine if any class of the prismatic rays have the power of exciting or destroying the phosphorescence in living animals. It would appear from the experiments of Becquerel, that the luminous and calorific rays should possess that power. That artificial heat interferes with the phenomena in organised bodies is very certain. The whole question, however, is one of great difficulty, but it is an inquiry which is calculated to clear up much of the

\* See Goethe's Optics.

doubt which exists at present as to the theories of the emission of luminous particles, and the excitement of an all-pervading luminiferous ether.

Similar phenomena have been noticed in the vegetable world. The leaves of the *œnothera macrocarpa* exhibit phosphoric light when the electrical intensity of the air is high. The *agarics* of the olive-grounds of Montpellier are often luminous at night. In the coal mines, near Dresden, the *rhizomorpha phosphoreus* shines with great brilliancy. Many of the lichens indeed are stated to possess this peculiar phosphorescent property; and from the circumstance of their existing in dark caverns, they appear to prove the conductibility of the luminous principle through masses of matter, or the power of production dependent upon vital force.

## CHAPTER IX.

## INFLUENCE OF THE SOLAR RAYS ON CHEMICAL COMBINATION.

(461.) ALREADY, in the first part of this work, several examples, which show the influence of the sun's rays upon combination, have been brought forward: a few instances of a remarkable kind remain to be noticed. Vogel observed, that if chlorine was passed into alcohol nearly saturated with that gas, and at the same time exposed to the sunshine, each bubble of chlorine, as it entered the spirit, exploded, giving a bright purple flame and a white vapour. This experiment I have repeated, and found that the effect depends entirely upon the agency of the chemical radiations. The interposition of an orange glass, or a yellow fluid, is quite sufficient to stop this energetic chemical combination.

(462.) It has long been known to chemists, that a mixture of chlorine and hydrogen gases might be preserved in darkness, without combining, for some time; but that exposure to diffused daylight gradually occasioned their combination, whilst the direct solar rays produced the sudden inflammation of the mixture. This combination has been investigated by Gay Lussac, and Thenard, and also by Davy. Sir Humphry Davy states that a mixture of chlorine and hydrogen acted more rapidly upon each other, *combining without explosion*, when exposed to the red rays, than when placed in the violet rays. But he found that a solution of chlorine in water, became a solution of muriatic acid most rapidly, when placed in the most refrangible rays: the former statement is doubtful.

(463.) My own experiments appear to show that the combination of these gases may be effected in every part

of the prismatic spectrum, but that it is entirely independent of the luminous rays. I have kept chlorine and hydrogen without uniting, behind a yellow medium, for as long a period as I have been able to preserve the mixture in the weakest diffused daylight. It does not, however, appear to be quite independent of calorific influence; for I find that the combination is effected gradually under the influence of the dark rays of heat.

(464.) We have evidence to show that the chemical agent, whatever it may be, which accompanies Light, is diffused over every part of the prismatic spectrum, although its action is modified by the luminous and calorific influences. Now, as it is proved that a very small amount of actinic power will occasion the chemical combination of these gases, we can well understand that it is diffused over the whole of the rays, although in different degrees. Dr. Draper has shown that the Light of a taper produces a decided effect upon the mixed gases, chlorine and hydrogen, and also that the Light emitted during the rapid passage of the electric spark, acts powerfully upon them. "For speed of action no *tithonographic*\* compound can approach it; a Light which perhaps does not endure the millionth part of a second, affects it energetically." In the red ray the chemical influence is pretty active, and this, combined with the thermic power of that ray, accounts for the phenomenon observed by Davy. I have found, however, that the combination is effected with the greatest speed by the extreme blue and the indigo rays. Dr. Draper has fixed the maximum in the indigo rays, and giving a numerical value to the forces exerted by the different rays, he calls the maximum power of the

\* Tithonicity was a name given by Dr. Draper to the chemical rays; but which is, it appears to me, badly chosen; and certainly not at all in accordance with the Lavoisierian principle of nomenclature, which teaches, that the *word* should give birth to the *idea*, the idea depict the *fact*.

Indigo ray	-	-	-	-	240·00
Blue ray	-	-	-	-	144·00
Violet ray	-	-	-	-	121·00
Green ray	-	-	-	-	54·00
Extra spectral rays	-	-	-	-	12·00
Yellow ray	-	-	-	-	2·75
Orange ray	-	-	-	-	·75
Red ray	-	-	-	-	·50 ?

The red ray should have a much higher power than is here stated; I have found it quite equal to the green ray, and, I think, superior to it in effect. I should remark that, by using glass tubes of small bore, we secure the combination of the gases without any explosion.

(465.) Taking advantage of the action of the sun's rays upon these gases, Dr. Draper devised an instrument for measuring the chemical force exerted by Light. This instrument consists essentially of a mixture of equal volumes of chlorine and hydrogen, which is evolved from, and confined over muriatic acid, in a graduated bent tube. The gases are liberated from the liquid acid by the agency of galvanic electricity. Platinum wires, which can be connected with a voltaic battery, are inserted into the tube in such a manner, that when the required quantity of the gases is formed, the decomposition ceases, owing to the fluid having fallen below the wires. The gases combine in a longer or shorter time, according to the amount of Light; the number of degrees over which the fluid falls in the graduated arm in a minute giving relatively the force in action. This instrument is certainly a very ingenious application. But it appears to me, there are so many causes which will operate to produce an irregular action, that the results obtained by such an instrument can only be received as approximations to the truth, and indeed not that, unless the average of a great many carefully conducted experiments be taken in every case.

(466.) The formation by the sun's rays of precipitates which do not occur in the dark, has engaged the attention of Sir John Herschel; but further investigations

are required. A few examples will be found in a future paragraph.

(467.) Phenomena which I have observed lead me to believe that under no circumstances, where the changes are gradual, does precisely the same thing take place in darkness as in daylight.

As far as my own observations have gone, I find that in all cases where precipitation does not take place immediately upon mixing two solutions, there is a very marked difference in the time required for precipitation to ensue in a fluid kept in the dark, and one exposed even to diffused daylight, this being, of course, more strikingly shown if one fluid is placed in the sunshine. Some interesting experiments illustrating this part of the subject will presently be given.

(468.) Chlorine, iodine, and bromine, it is well known, act with considerable energy upon metallic bodies. If, however, any polished metal is exposed to the action of them in a diluted state, the combination is, at first, exceedingly weak, and the films that are formed by either of these three elementary bodies, upon any metal, undergo considerable change under the influence of the sun. In most cases it appears that these bodies are set free, and the metal left in a state of very fine division or oxidisation. Copper, tin, iron, zinc, lead, pewter, bismuth, and several other metals have afforded the same results. It is still more remarkable, that films of bromine or iodine on glass are found, under the action of the sun, to act in a similar manner; and in 1841 I published an account of the power of iodine in rendering wood capable of receiving photographic images.

(469) In connexion with this section of my subject, the following observations and experiments of Dr. Frankland are most important. They are abstracted from his "Researches on the Organic Radicals," published in the Quarterly Journal of the Chemical Society.

"Scheele, Seebeck, and others, found that nitric acid



exposed to sunlight, is converted into nitrous acid and oxygen, whilst many metallic oxides lose the whole or a part of their oxygen: thus, peroxide of lead is resolved into minium and oxygen; grey oxide of mercury into metallic mercury and red oxide; whilst red oxide of mercury, under water, is decomposed into grey oxide and oxygen gas. \* \* \* \*

(470.) "It has been long known, that certain inorganic bodies, containing iodine, such for instance as the iodides of silver and gold, undergo decomposition when exposed to light; the iodine compounds of the noble metals, appearing to be most susceptible of this change. From the close relation of hydrogen to these metals, its iodide might be expected to possess the same susceptibility, and this is, in fact, found to be the case; for it is well known, that aqueous hydriodic acid, even when preserved in closely stopped bottles, gradually turns brown on exposure to light, from the separation of free iodine, but the decomposition only becomes continuous when the iodine is removed as fast as it is liberated; it has also been observed, that when hydriodic acid gas is allowed to stand over mercury, its volume becomes reduced to one half, and the residual gas consists of pure hydrogen; but whether this reaction only occurs under the influence of light, has not been clearly established.

(471.) "It has been remarked by almost all chemists who have had occasion to employ iodide of ethyl, that this liquid becomes brown, from the separation of iodine, when exposed even to diffused daylight; this observation, which I have myself of late also frequently had an opportunity of making, induced me to hope that a decomposition here occurs analogous to that suffered by the iodide of hydrogen under the same influence. I find that the ethyl compound, when exposed to direct solar light, rapidly becomes of a dark-brown colour; but, as is the case with hydriodic acid, this separation of iodine soon ceases, and when a certain intensity of colour has been attained, no

further action takes place; if, however, the free iodine be removed by agitating the liquid with mercury, the action immediately recommences, and proceeds to the same point as before. This behaviour of the iodide under light, and in contact with mercury, indicated the method by which the action could be carried on continuously, and the products collected and preserved.

(472.) "For this purpose several glass flasks, of about 10 ounces capacity, were filled with mercury, and inverted in a vessel containing the same metal; a few drops of iodide of ethyl being then introduced into each, by means of a pipette, they were exposed to the direct rays of the sun. The surface of the mercury, where it was in contact with the liquid, soon became covered with a film of protoiodide, which by the further action of the light, was converted into biniodide, whilst bubbles of gas were continually evolved, and gradually displaced the mercury from the flask; finally, the whole of the iodide of ethyl disappeared, the gas and biniodide being the sole products of the decomposition. Although simple exposure to the sun's rays caused this action to take place with tolerable rapidity, yet it was greatly accelerated by placing each flask near the focus of an 18-inch parabolic reflector, which was not, however, so highly polished as to cause a very considerable elevation of temperature, the heat never rising to the boiling point of iodide of ethyl. (71.6° C.)  
\* \* \* \*

(473.) "As iodide of ethyl is not in the least acted upon by mercury, at a temperature of 150° C., it could scarcely be supposed that the comparatively low degree of heat to which these materials were exposed in the focus of the reflector, could play any important part in the decomposition; yet, in order to set the question entirely at rest, an inverted bell-jar, containing iodide of ethyl, confined over mercury, was surrounded by a glass cylinder, and this latter filled first with water, then with a solution of chloride of copper, and lastly with a solution of

bichromate of potash. When the outer cylinder was filled with water, the decomposition proceeded with as much rapidity as without the intervention of that fluid, whilst the temperature of the water was scarcely perceptibly raised during the operation, the same was the case when solution of chloride of copper was employed; but on substituting the solution of bichromate of potash, *scarcely the slightest action was perceptible, even after several days exposure to bright sunshine.* Now since, according to Mr. Hunt, at whose suggestion I employed these liquids, the solution of chloride of copper absorbs nearly all the heating rays, and allows about 90 per cent. of the actinic rays to pass, whilst the solution of bichromate of potash intercepts the actinic, and gives free passage to the heating rays,—it is evident that the decomposition before us is due to the chemical influence of light, and is totally independent of the heating rays of the solar spectrum."

(474.) INFLUENCE OF THE SOLAR RAYS ON PRECIPITATION. —In 1832 Sir John Herschel communicated the remarkable fact, that when a solution of platinum in nitro-muriatic acid, which has been neutralized by the addition of lime, and has been well cleared by filtration, is mixed with lime-water in the dark, no precipitation, or scarcely any, takes place, but when (being thoroughly cleared of any sediment) this mixture is exposed to sunshine it instantly becomes milky, and a white or yellowish-white precipitate speedily falls.

By exposing this mixture behind coloured media, Sir John Herschel found that the effect was due to the influence of the most refrangible rays. I have placed this mixture in small glass tubes, and so arranged them that they were individually exposed to a separate ray of the spectrum. After an exposure of one hour the following results were obtained, the precipitates having been carefully washed and dried in the tubes in which they were formed.

Most refrangible rays beyond the visible spectrum	0.07 gr.
Violet rays - - - - -	1.05 „
Indigo rays - - - - -	0.60 „
Blue rays - - - - -	0.45 „
Green rays - - - - -	0.10 „
Yellow and orange rays - - - - -	-
Red rays - - - - -	0.05 „

It is a fact worthy of especial notice, that this precipitation is so dependent upon the amount of sunshine, that precipitates obtained in the same time, being carefully weighed off, will show the relative amounts of actinic influence to which they have been exposed.

(475.) *Manganate of Potash*.—A solution of this body having been made in the dark, was placed in two glass vessels, and set aside. After having been kept in darkness for two hours, the solutions remained as clear as at first. One of the vessels with its contents was then removed into the sunshine, when the solution immediately became cloudy, and was very speedily decomposed, the precipitate falling heavily. By experiments with the spectrum, I have since found that the precipitation is due almost entirely to the more refrangible rays. I have not been enabled to decide with that degree of accuracy I could desire, in which ray the maximum effect is produced. The precipitates formed in the blue, indigo, and violet rays were nearly of the same weight, but it did appear that the precipitation was most *speedily* produced by the mean *blue* ray.

If we dissolve the brown precipitate from the mineral chameleon in a solution of cyanide of potassium, we have a clear fluid. Reserve one portion in darkness, and expose another to good sunshine, the solution preserved in the dark will remain quite clear for many days, whereas that exposed to actinic influence throws down a brown precipitate after a few hours' exposure. If the solution is washed over paper, we procure by exposure good negative images of leaves or any other body superposed.

(476.) A few grains of sulphate of the protoxide of iron

were dissolved in rain water. If kept in perfect darkness, the solution remains clear for a long time; it becomes, however, eventually cloudy and coloured from the formation of some basic salt of iron, even in tubes hermetically sealed. A few minutes' exposure to sunshine is sufficient to produce this change, and the salt formed, instead of floating in the fluid, and as in the former case rendering it opaque, falls speedily to the bottom.

(477.) Some years since, at the Meeting of the British Association at Plymouth, I published an account of an exceedingly sensitive photographic process, the agents employed being iodide of silver and the ferro-cyanide of potassium. I have since then made some experiments with the hope of ascertaining the rationale of the chemical changes which take place. This has not been done in anything like a satisfactory manner; they have, however, led me to observe a curious effect produced in mixed solutions of iodide of potassium and ferro-cyanide of potassium under the influence of sunshine. If a mixture of these salts is kept in the dark, no change takes place for a long period, but if exposed to sunshine, the colour of the solution is much deepened, becoming of a bright golden yellow, and a light brown powder is precipitated. This precipitate has not been analysed, other than qualitatively; but I believe it to be a combination of iron and iodine, and I have good reason for supposing that a very remarkable change takes place in the arrangement of the elements of the salts employed.

(478.) 100 grains of the protosulphate of iron were dissolved in 2 oz. of distilled water; 30 grs. of the bichromate of potash were dissolved in 4 oz. of distilled water; 1 oz. of the iron solution was weighed into two large test-tubes, and 6 drachms of the solution of the bichromate of potash added to each, which formed a fine red-brown clear solution. One tube was kept from all light, and the other exposed to good sunshine for an hour; in both tubes there was a precipitation of the chromate of iron, described by

Dr. Thomson in his memoir on the Salts of Chromium, published in the Philosophical Transactions. The solutions, which were perfectly clear, were poured off from the precipitates; these were washed and weighed. The precipitate formed in the dark was found to weigh three grains more than that formed in the sunshine. This result was different from what my previous experiments had led me to expect, and it was several times repeated with the most scrupulous care. In every instance the precipitation which took place during *the first exposure* to sunshine was less than that formed in darkness.

(479.) The clear actinized solution poured off from the chromate of iron, being again exposed to solar influence, the other being carefully guarded from the slightest radiation, it was found that the precipitation went on much quicker in sunshine than in the dark; the side of the tube facing the sun was always thickly coated with chromate of iron, whilst the other side of it was perfectly free from any precipitation. Dr. Thomson has shown that this precipitation is produced by heat; it became interesting to know what part solar heat had in the phænomena. As I experienced some difficulty in arranging in a satisfactory manner many tubes along the prismatic spectrum, I used only three. One was placed in the mean indigo ray, another in the mean yellow ray, and the third in the least refrangible red ray. After an exposure of four hours, the precipitation formed in the tubes in the different rays were as follows:—

Indigo ray	-	-	-	5.25
Yellow ray	-	-	-	0.50
Red ray	-	-	-	2.15

Similar results were obtained by placing the solutions behind blue, yellow, and red glasses, proving that although the calorific rays were not without action, the principal effect was due to the chemical rays. The half-grain formed in the yellow ray I still regard as due to the

thermic or actinic power of the beam, as behind a deep-coloured yellow solution (sulphate of potash and chromium) no precipitate was formed in eight hours.

(480.) I have made one or two other experiments (particularly one with a mixture of the bichromate of potash and the sulphate of copper) in which precipitation appears retarded by solar agency. I am rather inclined to think that it will eventually be proved that the electric energy of the different bodies in relation to each other will greatly modify the results we shall obtain in these experiments, and I intend, if possible, to investigate this part of the subject with care. Since Becquerel has shown (*Annales de Chimie*, November, 1843) that the electrical excitation produced by the solar rays is different for each ray, and that this power is at its maximum in the yellow ray and also in the violet ray, the minimum force being between the green and blue rays; and since the mean maximum of chemical energy has been shown to manifest itself in the violet ray, and its minimum invariably to reside in the yellow ray; and as it is known that the negative and positive currents or sparks produce opposite effects, may we not reasonably conclude that the solar radiations are in some remarkable manner involved in the production of electrical phenomena? To say, as has been said, that electricity is the agent producing the effects I have been considering, is rushing much too hastily to a conclusion; indeed, cases will be found in which, at the maximum of electrical power in the spectrum, electrical phenomena which would occur in darkness or in light, apart from heat or actinism, are entirely prevented.

(481.) COLOUR OF PRECIPITATES.—If a solution of bichromate of potash is exposed to sunshine, it acquires a property of precipitating several metals as chromates, differing many shades in colour from the colours produced by a similar solution prepared and kept in the dark. If the actinized solution be poured into a solution of nitrate of silver, the chromate of silver formed is of a much more

beautiful colour than that given by a solution which has not been exposed to the sun. A like effect will take place in precipitating chromate of mercury with actinized and non-actinized solutions of the chrome salt.

Solutions of sulphate of iron exposed to sunshine, yield a Prussian blue with the ferro-cyanide of potassium, of a far more beautiful colour than that produced by a solution which has not been so exposed. If solutions of both the salts are kept for many hours in good sunshine, the colour of the resulting Prussian blue is still improved.

I have long noticed in the process of darkening photographic papers and Daguerreotype plates, that the colours produced varied in richness of tint and in shade with the brightness of the sun and the clearness of the atmosphere at the time of exposure. In some positive processes, in which a darkened paper was bleached under the influence of actinic radiations (if this expression be permitted), the effects of colour were often very striking and beautiful, whereas in winter, or when a slight haze existed, a dull dun-brown almost invariably resulted. It appears that dyers and the manufacturers of some of the fine pigments are not unacquainted with these facts; they are certainly curious, and deserve attentive investigation at the present time. I regret that I am only in a position to record the facts I have noticed, not having as yet determined even the influence of the various independent rays upon these coloured precipitations.

(482.) ACTINIC INFLUENCE IS PROBABLY ABSORBED. — Two phials were filled with a solution of acetate of silver and carefully corked. One was exposed for an hour to good sunshine, whilst the other was carefully kept in the dark. At the end of this time, a solution of the protosulphate of iron having been made in the dark, ten drops of it were added to each solution of silver. The one which had been exposed gave *immediately* a copious precipitate of silver, whereas the other was only rendered slightly turbid, and was some minutes before it precipitated.



After having stood eight or ten minutes no difference could be detected in the quantity of silver precipitated in either phial.

Acetate of mercury was used in the place of the acetate of silver, and the difference between the actinized solution and the other, on the addition of the iron salt, was very striking.

The two salts, acetates of silver and mercury, were mixed (they had been used combined, rather successfully in a photographic process of some interest). One portion was exposed in a large test-tube carefully corked, and another portion was protected from all light in a bottle. The exposure in this case was from two to three hours but during that time there was not more than half an hour's good sunshine. By the light of a taper an equal quantity of the sulphate of iron was added to each. In about three minutes the solution which had been exposed appeared a little disturbed, small specks were seen to form in various parts of the fluid, and these rapidly increased in size and assuming star-like shapes, fell heavily. At the expiration of an hour a dark and bulky precipitation was formed, but in the unexposed solution the precipitate was but little and of a light gray colour. In about two or three hours a coating of white metal was formed in two well-defined stripes along the tube which had been under solar influence; one on the side directly facing the sun, and the other on the other side of the tube, but along a line, upon which I found by subsequent experiment the rays were concentrated, by the form and refractive power of the media—glass and metallic solution—through which they had to pass. That these lines were due to the action of the solar rays was proved by placing a piece of blackened paper around a tube, during exposure, which effectually prevented the metallic deposit over the space covered. This deposit is somewhat capricious in its formation. The experiment has been often repeated, but although the precipitation was invariably as described,

frequently happened that no metal was deposited along the glass.

(483.) Sulphate of iron in solution was found to acquire the same property by exposure as the other salts above-named. 30 grs. of this protosalt were dissolved in an ounce and a half of water. It was then divided into two portions, one of which was exposed for an hour to sunshine. 100 grs. of each solution were carefully weighed into test-tubes, and the same weight of a solution of nitrate of silver made in the dark, was added to each. As quickly as possible the precipitates were collected, washed, dried and weighed. The precipitate produced immediately by the iron solution which had been actinized weighed 2·8 grains, whereas the precipitate by the unexposed solution weighed 0·7 grain. These results are the mean of six experiments.

(484.) Two test-tubes had 120 grains of an actinized solution of nitrate of silver weighed into them, and into two others was put the same quantity of a like solution which had not been actinized. Four other tubes held the same weights of solutions of the protosulphate of iron, two of them actinized, the others not so. They were mixed in the following order, and the precipitates collected immediately from each were as stated:—

1. Actinized silver with actinized iron -	0·5 gr.
2. Unactinized silver with unactinized iron -	0·7 „
3. Actinized silver with unactinized iron -	1·0 „
4. Unactinized silver with actinized iron -	1·5 „

Considerable difficulty arises from the length of time which must necessarily elapse before the precipitates can be removed from the solutions. In all cases I find that after some little time the conditions required to effect a precipitation are established, and in both kinds of solutions it then proceeds without any apparent difference. It would appear from the above results, which are the mean of many experiments, that when both solutions are brought

into the same actinic condition they do not precipitate more freely than those do which have been kept in the dark. It appears to be necessary that the actinic states should be dissimilar to ensure the production of these curious phenomena, which evidently point to some law of chemical action which has not yet been made the subject of study.

(485.) Bichromate of potash, it is well known, is decomposed by the agency of the solar rays when in contact with organic matter. A solution of this salt spread upon paper forms a photographic agent of some interest. The paper, which is of a fine yellow colour when first prepared, becomes brown upon exposure to the sunshine, from the chromic acid of the salt being acted upon by the organic matter of the paper. A similar change takes place, to a certain extent, in solutions of this salt in distilled water, when exposed in clear glass vessels, for some time, to bright sunshine. The evidence we have of this is the gradual formation of minute bubbles of air, which are redissolved, and the progressive increase of free chromic acid in the solution, which may be detected by any of the usual methods.

A combination of the bichromate of potash and of sulphate of copper, either on paper or in solution, exhibits the above change very clearly, in the gradual formation of a chromate of copper of a peculiar character, which, although brown at first, becomes nearly white by prolonged exposure to solar influence; indeed, upon paper the whiteness is quite complete. Some very remarkable changes have been detected in combinations of these salts, which require further examination than they have yet received.

(486.) From two sets of experiments, on the electro-chemical action of the solar rays, I draw these conclusions:—

1st. That electro-metallic precipitation is prevented by the influence of the sun's rays.

2nd. That light is not the retarding agent, but that the

exercise of electrical force is negated by the direct influence of actinism.

I placed in a test-tube a strong solution of nitrate of silver; in another tube, this being closed at one end with a thin piece of bladder, I placed a solution of iodide of potassium; which was supported in the solution of nitrate of silver, by being fixed in a cork, and a piece of platina wire was carried from one solution into the other. An arrangement of this kind was kept in the dark; iodine was liberated in the inner tube, and a crystalline arrangement of metallic silver was formed around the platina wire in the outer one. A similar arrangement was placed in the sunshine. Iodine was liberated in the inner tube, but no silver was deposited.

Having exposed the above solution to the sunshine of July during a long day, the tube was placed in a dark cupboard, but the actinic influence which had been exerted on the solution of silver had produced a permanent change in its condition; after several days no trace of any metallic deposit could be detected, but the whole of the iodine again entered into combination, whereas this was not the case in the unexposed glasses.

In the inner tube I placed the solution of silver, and in the outer one the hydriodate of potash. One arrangement was kept in the dark, the other was exposed to good sunshine. In both instances the liberated iodine gave an intense yellow to the solution, and in both cases the quantity of metallic silver deposited was precisely the same.

This yellow fluid being analysed by the prism, was found to obstruct all the rays above the green, whilst it permitted the permeation of the yellow and orange rays in great quantity and power. It is therefore evident that the luminous rays of the solar spectrum have no power in retarding electro-chemical action.

(487.) The following experiment gives a pleasing illustration of the excitation of electric currents by solar agency, and their opposition to ordinary chemical action.

Precipitate with any iodide, silver, from its nitrate in solution, and expose the vessel containing it, liquid and all, to sunshine; the exposed surfaces of the iodide will blacken: remove the vessel into the dark, and, *after a few hours*, all the blackness will have disappeared. We may thus continually restore and remove the blackness at pleasure. If we wash and then well dry the precipitate, it blackens with difficulty, and if kept quite dry it continues dark; but moisten it, and the yellow is restored after a little time. In a watch-glass, or any capsule, place a little solution of silver; in another, some solution of any iodine salt; connect the two with a filament of cotton, and make up an electric circuit with a piece of platina wire: expose this little arrangement to the light, and it will be seen, in a very short time, that iodine is liberated in one vessel, and the yellow iodide of silver formed in the other, which blackens as quickly as it is produced.

Place a similar arrangement in the dark; iodine is slowly liberated. *No iodide of silver is formed*, but around the wire a beautiful crystallisation of metallic silver. Seal a piece of platina wire into two small glass tubes; these, when filled, the one with iodide of potassium in solution, and the other with a solution of the nitrate of silver, reverse into two watch-glasses, containing the same solutions; the glasses being connected with a piece of cotton. An exposure during a few hours to daylight will occasion the solution of the iodine salt in the tube to become quite brown with liberated iodine: a small portion of the iodide of silver will form along the cotton, and at the end dipping in the salt of silver. During the night the liquid will become again colourless and transparent, and the dark salt along the cotton will resume its native yellow hue.

(488.) M. Edmond Becquerel, in 1839, first called attention to the electricity developed, during the chemical action excited by solar agency. He provided a

blackened box divided by a diaphragm into two cells; in each cell he placed the fluid to be examined, and plates of platina or gold were dipped in each, and connected with a galvanometer. The cells being filled with acidulated water, and platina plates in each cell, it was found that when the red, orange, yellow, or green rays fell upon the fluids, no action was excited. The blue and indigo induced a feeble action, but a very decided deflection of the galvanometer was produced by the impact of the violet rays. In 1840, I repeated the experiments of Becquerel, with many modifications, using tubes bent into the form of **U**; or floating one photometric fluid upon another. The results I then arrived at completely confirmed those of M. E. Becquerel; and I was led to adopt this method of measuring the permeability of bodies to the "chemical rays."\*

(489.) Becquerel supposes the light to act on the corpuscles adhering to the surfaces of the plates. It is very convincingly proved that none of this excitement is due to calorific action. With an arrangement similar to that just described, the following results were arrived at by Becquerel when using screens of glass:—

Screens.	Intensity of Current.		Effects.
Without a screen	-	35·5	- 100
Violet glass -	-	9	- 27
Blue glass -	-	10·5	- 31
Green glass -	-	1	- 2·5
Yellow -	-	6·5	- 10·5
Red -	-	1	- 2·5

Here the incorrect results obtained by coloured glasses are very decidedly shown. All yellow glasses are permeable to some chemical rays; therefore, the intensity of 6·5 is to be attributed to these, and not to the luminous rays themselves. A plate of polished brass being exposed under similar conditions in various parts of the spectrum, the following results were obtained:—

\* See Philosophical Magazine, February, 1840.

Rays.		Intensity.
Red	-	- 1
Orange	-	- 0
Yellow	-	- 2
Green	-	- 4
Blue	-	- 2
Indigo	-	- 0
Violet	-	- 0

Here it would appear that the maximum effect was produced by the green rays.

The plate of brass being oxidised the effects were as follows: —

	Intensity.	Effect.
Without a screen	- 4·5	- 100
Violet glass	- 2	- 44·5
Blue	- 1	- 27
Yellow	- 0	- 0

Plates exposed to iodine, chlorine, and bromine, were tried by M. E. Becquerel, and similar results obtained.

(490.) Not considering these results so satisfactory as I could desire them to be, I instituted during the summer of 1843 a series of experiments with plates of different metals, which were excited in several ways. These plates were connected with wires from the galvanometer, the different prismatic rays were passed separately through a slit in a card, and the transient and permanent deflections carefully noted. The galvanometer, which was by no means a sensitive one, was never deflected by any ray below the green, unless by the extreme red, and this was no doubt a thermo-electrical action; but in the green a weak action was always detected, which increased powerfully as we ascended into the rays of still greater refrangibility; the maximum shifting with the kind of preparation employed, between the mean blue ray and the most refrangible violet.

(491.) This action is only to be regarded as one of the evidences of chemical disturbance, exciting electrical currents; yet at the same time, it opens the question of the identity of the agent producing this disturbance and

electricity. In the present state of the inquiry, we are bound to regard Light, Heat, and Electricity, as distinct elements; and possibly we have now to add a fourth to this list of imponderable agents. In the examples already brought forward in this treatise, we see the extreme difficulty which exists in keeping separate from each other the Light, Heat, and ACTINISM of the solar rays, and the results just stated, involve the element of Electricity in the already complicated consideration.

A few experiments made more recently with a sufficiently delicate galvanometer, prove that every ray of the spectrum produces an electrical disturbance. The rays, however, at the least refrangible end, produce a deflection of the needle in one direction, whilst the most refrangible rays set up a disturbance in an opposite direction. There are many indications of a condition analogous to polarity in the action of the prismatic rays.



## CHAPTER X.

## MAGNETISING POWER OF THE SOLAR RAYS.

(492.) HAVE the sun's rays the power of developing the phenomena of polarity in steel? This question has been agitated for upwards of twenty years. Dr. Morichini was the first to announce, that the violet rays of the solar spectrum had this power. The experiments were tried by collecting the violet rays in the focus of a convex lens, and exposing one half of fine needles, previously proved to be entirely free of magnetism, to the influence of these rays for half an hour. MM. Carpa and Ridolfi repeated these experiments of Morichini with the most satisfactory results, and the Italian philosopher succeeded in magnetising several needles, before Professor Playfair, and others. It must, however, be stated that Berard, Professor Configliachi of Pavia, and Dr. Faraday failed in producing the same effects. Mrs. Mary Somerville restored the confidence of the scientific world in the results of Morichini, by a series of exceedingly beautiful experiments which were published in the "Philosophical Transactions," for 1826. Needles were ascertained to be entirely free of magnetism; they were then half covered with paper, and the exposed end placed in the violet ray of the spectrum, about five feet from the prism. In two hours, the needle was magnetised, the exposed end being the north pole. The indigo ray gave nearly the same result. The magnetic influence was imparted by the blue and green rays, but in a much less degree. The yellow, orange, and the calorific rays were tried for several days; but no magnetism was developed. Pieces of clock and watch springs gave similar results. It was also found

that the same effects could be produced by exposing needles partly covered with paper to the Light which permeated cobalt blue and green glasses. Green and blue riband produced similar changes.

Baumgartner, of Vienna, discovered that a steel wire, polished in some parts and oxidised in others, became magnetic, exposed to the *white light* of the sun, the polished part becoming the north pole. The concentrated rays acted more rapidly, and in this way eight poles were obtained on as many inches of wire.

(493.) Barlocchi and Zantedeschi found that an armed natural loadstone had its power nearly doubled in twenty-four hours, if exposed to the strong Light of the sun, and that an artificial magnet which carried  $13\frac{1}{2}$  oz. supported  $3\frac{1}{2}$  oz. more, after three days' exposure to sunshine; and it at last supported 31 oz. by continuing the solar action. Zantedeschi found that while the strength increased in oxidised magnets, it diminished in those highly polished. He also discovered that by concentrating the sun's rays, the magnet *acquires strength* when its north pole is exposed to them; and *loses* it when their south pole is acted on by them.

(494.) Mr. Christie found that when a magnetised needle, or a needle of copper, or of glass, vibrated by the force of torsion in white Light, the arch of vibration was more rapidly diminished in the sun's Light than in the shade; this effect being more evident on the magnetised needle.

(495.) Riess and Moser \* published a series of experiments conducted with great care, which seem to throw much doubt on the results of other philosophers. They examined the number of oscillations performed in a given time, before and after the needle was submitted to the influence of the violet rays. A focus of violet Light concentrated by a lens, was made to traverse one-half of the

\* Edinburgh Journal of Science, New Series, No. IV. p.225.; Annales de Chimie et de Physique, November, 1829.

needle 200 times. They, however, could not detect any difference in the oscillations, which could be at all attributable to any magnetising property of the solar rays. These experiments were tried at different seasons of the year, and at all hours of the day. They also endeavoured to verify the results of Baumgartner, but without success.

(496.) Connected with these researches, there appear to be many almost inexplicable phenomena, which have probably led to these discordant results. The whole series certainly require a fresh investigation. Mr. R. W. Fox, in pursuing his investigations on terrestrial magnetism, was led to observe the fact, that the oscillating needle was much affected by the sun's rays; the arch of vibration being more rapidly diminished, as was observed by Mr. Christie. These experiments were repeated by Mr. W. Snow Harris, who adopted the plan of swinging the needles in a vacuum, and this talented electrician came to the conclusion that no such retardation took place, under the exhausted receiver of an air pump. It must, however, be borne in mind, that it is impossible to avoid the leaking in of air even with the best instruments; and this would give rise to currents which would materially influence the results.

(497.) Berzelius has stated that the results of Seebeck's experiments show, that in no circumstances do the sun's rays develop polarity in steel, which did not, previously to exposure to their influence, possess magnetic properties. He therefore considers the experiments of Mrs. Somerville as illusive.

(498.) I will now name an experiment of my own, and leave the matter for still further investigation. Twelve sewing needles were carefully examined, and found to be without any polarity whatsoever. These were stuck through four cards, and one half being thus screened from the Light, the other was covered with deep blue coloured glasses. Three of the needles were placed magnetic E. and W., and three others in the direction of the

dip of the needle. The other six needles were washed with dilute nitric acid, and arranged three on a card, in the same manner as the former. After having been exposed to sunshine for some hours, they were examined, and it was found that those needles which had been placed in the direction of the dip had acquired polarity; but no change could be detected in any of the others.

(499.) In 1845, Dr. Faraday communicated to the Royal Society a Memoir on the "Magnetisation of Light, &c.," and on the "Action of Magnets on Light." These subjects are intimately connected with our present consideration, and require some attention. Dr. Faraday's view will be best understood from the following note of explanation.

"Neither accepting nor rejecting the hypothesis of an ether, or the corpuscular, or any other view that may be entertained of the nature of Light; and, as far as I can see, nothing being really known of a ray of Light more than of a line of magnetic or electric force, or even of a line of gravitating force, except as it and they are manifest in and by substances; I believe that, in the experiments I describe in the paper, Light has been magnetically affected, *i. e.* that that which is magnetic in the forces of matter has been affected, and in turn has affected that which is truly magnetic in the force of Light: by the term magnetic, I include here either of the peculiar exertions of the power of a magnet, whether it be that which is manifest in the magnetic, or the diamagnetic class of bodies. The phrase 'illumination of the lines of magnetic force' has been understood to imply that I had rendered them luminous. This was not within my thought; I intended to express that the line of magnetic force was illuminated as the earth is illuminated by the sun, or, the spider's web is illuminated by the astronomer's lamp. Employing a ray of light, we can tell *by the eye*, the direction of the magnetic lines through a body; and by the alteration of the ray and its optical effect on the

eye, can see the course of the lines, just as we can see the course of a thread of glass, or any other transparent substance rendered visible by the light: and this was what I meant by illumination."

(500.) The order of the experiments will be understood from the following quotation:—"A ray of light issuing from an Argand lamp was polarised in a horizontal flame by reflection from a surface of glass, and the polarised ray was passed through a Nichol's eye-piece revolving on a horizontal axis, so as to be easily examined by the latter. Between the polarising mirror and the eye-piece, two powerful electro-magnetic poles were arranged, being either the poles of a horse-shoe magnet, or the contrary poles of two cylinder magnets; they were separated from each other about two inches in the direction of the line of the ray, and so placed, that, if on the same side of the polarised ray, it might pass near them, or, if on contrary sides, it might go between them, its direction being always parallel, or nearly so, to the magnetic lines of force. After that, any transparent substance placed between the two poles, would have passing through it, both the polarised ray, and the magnetic lines of force, at the same time, and in the same direction.

(501.) "Sixteen years ago, I published certain experiments made upon optical glass, and described the formation and general characters of one variety of heavy glass, which, from its materials, was called silicated borate of lead. It was this glass which first gave me the discovery of the relation between Light and Magnetism, and it has power to illustrate it in a degree beyond that of any other body; for the sake of perspicuity, I will first describe the phenomena as presented by this substance.

(502.) "A piece of this glass, about 2 inches square, and 0.5 of an inch thick, having flat and polished edges, was placed as a *diamagnetic* between the poles (not as yet magnetised by the electric current) so that the polarised ray should pass through its length; the glass acted as

air, water, or any other indifferent substance would do; and if the eye-piece were previously turned into such a position that the polarised ray was extinguished, or rather the image produced by it rendered invisible, then the introduction of this glass made no alteration in that respect. In this state of circumstances the force of the electro-magnet was developed by sending an electric current through its coils, and immediately the image of the lamp-flame became visible, and continued so as long as the arrangement continued magnetic. On stopping the electric current, and so causing the magnetic force to cease, the light instantly disappeared; these phenomena could be renewed at pleasure at any instant of time, and upon any occasion, showing a perfect dependence of cause and effect.

(503.) “The character of the force thus impressed upon the diamagnetic is that of *rotation*; for when the image of the lamp-flame has been thus rendered visible, revolution of the eye-piece to the right or left, more or less, will cause its extinction; and the further motion of the eye-piece to the one side or the other of this position will produce the reappearance of the light—and that with complementary tints, according as this further motion is to the right or left hand.

(504.) “When the pole nearest to the observer was a marked pole, *i. e.* the same as the north end of a magnetic needle, and the further pole was unmarked, the rotation of the ray was right-handed; for the eye-piece had to be turned to the right hand, or clock fashion, to overtake the ray, and restore the image to its first condition. When the poles were reversed, which was instantly done by changing the direction of the electric current, the rotation was changed also, and became left-handed, the alteration being to an equal degree in extent as before. The direction was always the same for the same line of magnetic force.”

(505.) A great number of substances, solid and fluid,

were employed. The polarised ray being passed through them while they were brought under the influence of powerful electro-magnetic force. Careful examination of all the results which Dr. Faraday obtained, go to prove, that some transparent medium is always necessary, and that, in the greater number of examples, the degree to which the line of light was affected by the magnet was exactly in proportion to the density of the medium. It would, therefore, appear, that the ray of light is not actually magnetised. The molecular arrangement of the medium through which the ray passes is altered, and consequently its refracting powers changed, and thus the effect on light is but secondary. We employ the light, indeed, to enable us to see the amount of change which takes place in the molecules of the transparent body. These results, which are of the most important character, and which serve to guide us in most difficult investigations, do not, therefore, appear to bring the relations of Light and Magnetism much nearer than they were previously to this investigation.

## CHAPTER XI.

## ANALYSIS OF THE SPECTRUM BY ABSORBENT MEDIA.

(506.) THE considerations to which this chapter is devoted are of the utmost importance, in both a philosophical and physical point of view. The inquiry is still necessarily incomplete, but two reports having been published by the British Association, it is thought advisable to include some notice of the experiments on which these are founded in the present volume.

The object in view is to determine, with all the accuracy possible, the relation which each coloured ray of the prismatic spectrum bears to the chemical action which takes place upon the different agents employed in the production of the sensitive surface. Since different media exhibit very various degrees of absorbent action upon the chromatic rays, as well as on the chemical rays, of the spectrum, by employing them we obtain indications by which we may determine the relation in which these phenomena stand to each other.

(507.) The plan upon which I am proceeding is this. Having obtained a very extensive series of coloured glasses, and, by the solution of chemical compounds, procured a still more varied set of transparent coloured solutions, I analyse the luminous spectrum of a well-formed vertical opening between two knife-edges, by passing the spectrum through a particular absorbent medium. The spectra are obtained, first, by means of an excellent flint-glass prism; again, by one of crown-glass of faultless purity, the manufacture of Messrs. Chance Brothers, of Birmingham; and, thirdly, by a hollow prism, in which I



have the means of employing fluids of very different refracting powers. For obtaining the chemical impression of the spectrum, I procure a flame-like chromatic image of great intensity, 1 inch in length, from a vertical opening in my steel plate. I have adopted this as my measure throughout, dividing it into 100 equal parts: thus, all the numbers employed are intended to express inches, or the one-hundredth part of an inch.

(508.) The photographic agents employed were the collodio-iodide of silver on glass plates, and the iodide of silver excited by gallic acid. All the first results were on the former preparation.

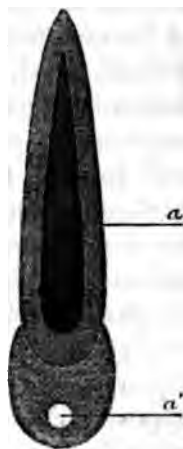
The collodion was made with gun-cotton which had been prepared with nitrate of potash and sulphuric acid. This being well washed, was dissolved in ether. Iodide of potassium was dissolved in spirits of wine iodide of silver added so long as it would take up any, and two drachms of this solution mixed with one fluidounce of the collodion. The solution of silver employed was thirty grains to the fluidounce of distilled water. The image was always developed by pyrogallie acid.

(509.) The NORMAL SPECTRUM was formed by a very pure flint-glass prism. — Light admitted between two knife-edges, separated  $\frac{1}{8}$ th of an inch, and generally passed through a hole of the same diameter in an inner screen. The chromatic image was received on a white tablet in a perfectly black box; its length, when most accurately adjusted, was 1 inch and  $\frac{3}{20}$ ths, but for convenience this has been reduced to 1 inch and divided into 100 parts, and relatively to this all the chemical spectra have been corrected (1:2).

*Without any interposed medium.* — Chemical action commences .40 above the lower end of red, and from this point extends to the length of  $1\frac{1}{2}$  inch. Over the space covered by the red and orange rays are indications of a well-defined circle of protective action; immediately above this a dusky brown commences, forming a kind

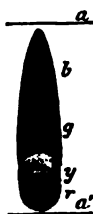
of fringing which is extended to  $\cdot 60$ , and in a similar manner it bounds the whole of the spectrum. This is due to diffused light, which I always find bordering the spectrum. Over a space equal to  $\cdot 10$  a well-defined black space appears, then the action weakens, but is still strong over  $\cdot 7$ , when it again increases just at the end of the violet, and is somewhat sharply cut off at  $1\cdot 90$  above 0, or lowest red, presenting an image similar to that represented in the margin.\*

In all the figures inserted, the lines  $a'$ ,  $a$ , mark the length of the unabsorbed normal spectrum.



(A.) *Series of Yellow Glasses.*

(510.) DEEP YELLOW. *Colouring matter Carbon.*—The ordinary red rays very intense, but partaking more of a scarlet colour from the mixture of yellow than a pure red; the orange and red rays blend so perfectly that it is difficult to define their boundaries. Combined, these rays occupy  $\cdot 12$ . The yellow rays are reduced to a line of bright light equal to  $\cdot 10$ . Beyond these the green rays appear very intense, and occupy a well-defined space equal to  $\cdot 25$ . Blue and violet rays, confined within a space equal to  $\cdot 38$ , appear somewhat more luminous than the green, presenting no decided colour, but appearing rather as a patch of a pale neutral tint.



(511.) *Chemical Spectrum.*—Chemical action commences

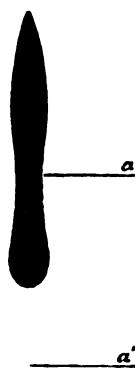
\* This description and drawing has been already given at page 144, but as it has direct reference to the experiments which are given in this chapter, it has been thought advisable, for convenience, to repeat it in this place.

over the region of the indigo and violet rays, the most intense action appearing to take place about the line H of Fraunhofer. It forms eventually a well-defined oval, the greatest amount of darkening going on in the centre of the impressed spectrum, a protected band, well-defined from the other parts of the surface, in contrast with the little darkening from extraneous light beyond the luminous image. The space between *a* and the lower end of the impressed spectrum is very decidedly protected from change. Upon placing the glass in a solution of hyposulphite of soda, and allowing it to remain for some time, the variations of action are more apparent:—1st, the very dark centre; 2nd, a band of much weaker action; 3rd, a far more energetic band surrounding the whole; and 4th, a protected band extending from the lower point far below this as a protected circle, as indicated by the shading in the figure.



(512.) MEDIUM YELLOW, *believed to be Charcoal*.—The red ray exhibits more crimson from the introduction of blue; orange and yellow well-defined; green ray somewhat shortened, but exhibiting considerable intensity, and well-defined. The blue ray reduced to a small band, and the rays beyond are only indicated by a pale stream of light, neutral in colour.

(513.) *Chemical Spectrum*.—Chemical action commences above the yellow ray, upon the confines of, but *in* the green, commencing  $\cdot 40$  above lower red, the space occupied by the green rays being impressed as a well-defined oval of the length of  $\cdot 25$ , then a neck of very much lower intensity of  $\cdot 20$ ; a large and well-defined oval  $\cdot 90$  in length, exhibiting the greatest degree of intensity in the middle space, shaded off to the edges. The length of



impressed spectrum 1·40, and from the zero  $a'$  to end of chemical action 1·85, or length of action beyond luminous spectrum at  $a$  ·85. Here we have an extinction of the violet and indigo rays; and over the space occupied by the blue rays a comparatively weak action, this action being continued with very much energy over the space occupied by the dark rays. The indication of protected spaces around the spectrum is less evident than in many other examples.

(514.) The CHEMICAL PREPARATION employed in the series of experiments which I have now to describe, was the iodide of silver as obtained on the ordinary iodized paper, rendered sensitive by the mixture of gallic acid and nitrate of silver. As, however, I find that nearly every variety of paper, and certainly every different manipulation, gives rise to an alteration in the scale of sensibility, it becomes important that I should describe exactly the character of the paper employed.

A very hard and uniform paper of Turner's was selected; its surface being beautifully pressed, and presenting a fine ivory character. It was first washed with a solution of sixty grains of nitrate of silver to the fluid ounce of distilled water, and dried; then with a solution of thirty grains of the iodide of potassium to the fluid ounce of water. After standing for a few minutes, each sheet was placed in a large vessel of water, and allowed to soak for about half an hour. After this, being hung by one corner, it was allowed to dry in a warm room; if the atmosphere was moist, at a short distance from the fire.

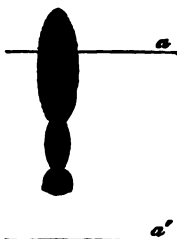
This paper was placed upon the screen on which the spectrum obtained fell, after it had been submitted to the action of the medium under examination. Everything being carefully adjusted, the paper was washed rapidly by a wide flat brush, with the following mixture:—

Saturated solution of gallic acid	-	-	-	40 drops.
Nitrate of silver, thirty grains to fluid oz. of water			10	„

The action was, in most cases, allowed to continue for a few seconds only, and the image developed itself slowly in the dark, without any subsequent application of the developing fluid.

(515.) *PURE YELLOW. Colouring matter Carbon.*—The visible spectrum is reduced by the violet and indigo rays; the orange blends with the yellow, which is consequently much extended (a slight extension arises also from the reduction of the green space); the illuminating powers of the outstanding rays are but very slightly diminished.

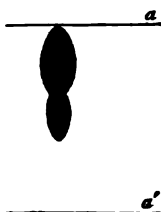
(516.) *Chemical Spectrum.*—Chemical action commences in the mean yellow ray about  $\cdot 20$  above  $a'$ ; it extends, in the first instance, over a space equal to  $\cdot 10$ , forming a patch of a semimetallic lustre with an olive-grey colour; this action is continued for another equal space, but the impressed space has more of a brown hue; these gradually blend into one nearly circular spot. From about  $\cdot 30$  above  $a'$ , a second action commences, independently of that already described; and indicating, as it appears to me, a set of rays of distinct character. Beyond this, at about  $\cdot 60$ , another oval forms, which continues and extends to  $\cdot 15$ , or sometimes, if the sun is very bright, to  $\cdot 20$  beyond  $a$ . This space, equal to  $\cdot 60$ , is in every respect very broadly distinguished from that which is produced between the lines C and F of Fraunhofer. It is characterized by a light cloudy brown colour, which deepens a little in colour beyond the luminous rays of the ordinary spectrum, when it is somewhat suddenly shaded off. The action may be well represented by two ovals, one considerably larger and longer than the other, which overlap; and it would appear that the change of colour, observed in the upper section of the lower space is due to this involved action of two sets of rays. In the chemical spectrum described, obtained after the ab-



sorptive action of a medium yellow glass, an indication of precisely similar peculiarity was obtained on the collodion plate, although at that time sufficient importance was not attached to the difference.

(517.) *YELLOW, by Iron.*—The least refrangible rays are scarcely at all influenced by this glass; the orange is slightly extended upon the red; and the yellow in a similar manner encroaches on the green rays. The green rays are, however, very decided, and beyond them there still appears an outstanding line of blue, or rather dark indigo; but beyond these no further rays are visible.

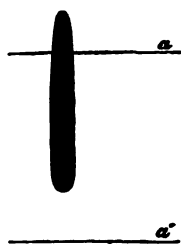
(518.) *Chemical Spectrum.*—At the most refrangible edge of the yellow rays the chemical action begins; and it may be at once described as extending to the very edge of the space occupied by the visible rays of the unabsorbed spectrum. In this, as in the spectrum from the carbon yellow glass (515.), a like dissimilarity was observable between the action of the two ends of the chemically active rays, although not to the same extent. The lower space, which commences about  $\cdot 40$  above  $a'$  and extends to above  $\cdot 60$ , is a pale gray spot, with a well-defined outline. The upper space, commencing at  $\cdot 55$  above  $a'$  and extending completely up to  $a$ , is much broader than the first, less perfectly defined, and of a brown colour of the same character as that already described. After several experiments, in which the periods of exposure were much varied, it was proved that no chemical action took place actually in the yellow rays when this glass was employed.



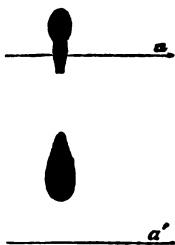
(519.) *STRAW-YELLOW. Silver Stain upon one Surface only.*—Shortens the spectrum by two-thirds of the violet, so that its entire length is reduced to  $\cdot 80$ ; the other rays continue unchanged, exhibiting a tolerable degree of intensity. When concentrated by a lens, the violet ray is

seen to suffer yet further extinction relatively to the other rays.

(520.) *Chemical Spectrum*.— Action commences at  $\cdot 20$  above  $a'$ , and extends over the more luminous space with the greatest intensity; then the action suddenly weakens over the limits of the green rays, growing more intense under the action of the blue and indigo rays. A still more decided weakening of chemical activity occurs at about  $\cdot 18$  below  $a$ , from which space unto  $\cdot 20$  beyond  $a$ , a faint indication of action is continued. Thus we have here two very remarkable maxima and minima; the former in the yellow and blue rays, and the latter in the green and violet rays, and beyond them.



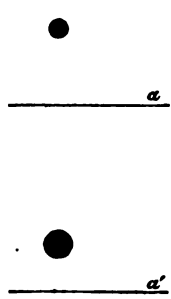
(521.) *MEDIUM YELLOW, believed to be Charcoal*.—The red ray exhibits more crimson from the introduction of blue; orange and yellow well-defined; green ray somewhat shortened, but exhibiting considerable intensity, and well-defined. The blue ray reduced to a small band, and the rays beyond are only indicated by a pale stream of light, neutral in colour. The chemical action on the iodized paper is limited to two well-defined spaces; one, the more intense, a dark oval over the point of greatest luminous intensity, equal to  $\cdot 20$ , commencing at  $\cdot 15$  above  $a'$ , and terminating at  $\cdot 35$   $a'$ . Between this point and the most refrangible violet there is no effect, the paper remaining quite unchanged; then at the extreme verge of the luminous spectrum a weak chemical action commences, which extends to  $1\cdot 20$ . This is singularly weak, except in the mean space about  $\cdot 10$  above  $a$ , where the influence of the chemical rays is more decided.



(522.) *ORANGE, Silver*.—All the more refrangible ordinary rays are very decidedly obliterated, and even the

green somewhat shortened; but in the place of the blue and violet rays there is observable some red. The yellow and orange are considerably reduced, the red standing out in great brilliancy.

(523.) *Chemical Spectrum*.—A very singular result is obtained when the prismatic rays are subjected to the absorptive action of this medium. A faint spot makes its appearance in the yellow space, and in the *point of maximum luminous intensity*. No other action than this occurs within the limits of the visible spectrum; but about  $\cdot 40$  beyond  $\alpha$ , a yet fainter spot of chemical action makes its appearance. Thus we have in this example evidence of two sets of chemical rays which have a very much greater penetrating power,—relative at least to the yellow media we have been examining,—than any of the others which are situated in those parts of the spectrum usually referred to as possessing the greatest chemical power. Other examples of a similar description will be noticed.



(524.) *ORANGE-COLOURED GLASS, Silver*.—Possessing in a remarkable degree the false dispersion observed by Mr. Stokes. It reflects from one side, when placed on a piece of black velvet, a peculiar bluish-green light; or when placed on a sheet of white paper, the scattered light partakes of that mixture of blue and brown which is ordinarily distinguished as a puce.

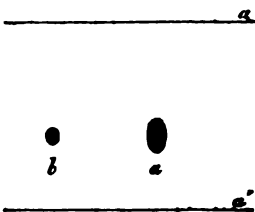
Of this variety of glass Mr. Stokes makes the following remarks in his memoir “On the Change of Refrangibility of Light”: —“Orange-coloured glasses are frequently met with, which reflect from one side, or rather scatter in all directions, a copious light of a bluish-green colour, quite different from the transmitted tint. In such cases the body of the glass is colourless, and the colouring matter is contained in a very thin layer on one face of the plate.”

This is not always the case; in the glass with which the present experiment was made, the colouring matter,



silver, is diffused throughout the mass. The peculiarity in question is produced on one surface by exposing it to the influence of the flame of burning wood.

Mr. Stokes continues:—"As this phenomenon was supposed by Sir John Herschel to offer some analogy with the reflected tints of fluor-spar and a solution of sulphate of quinine, I was the more desirous of determining the nature of the dispersion. It proved on examination to be nothing but false dispersion, so that the appearance might be conceived to be produced by an excessively fine bluish-green powder contained in a clear orange stratum, or in the colourless part of the glass immediately contiguous to the coloured stratum. The phenomenon has therefore no relation to the tints of fluor-spar or sulphate of quinine. It is true that the very same glass which displayed a superficial reflection of bluish-green, when examined by condensed sun-light exhibited also, in its colourless part, a little true dispersion, just as another colourless glass would do. But this has plainly nothing to do with the peculiar reflexion which attracts notice in such a glass." The spectrum transmitted through this glass is shortened by the loss of the violet, indigo, and nearly all the blue rays; some rays are, however, still visible beyond the green, which assume a reddish colour. The orange rays are extended into the yellow, with which much white light is mixed, and the least refrangible rays lose some of their illuminating power.

(525.) *Chemical Spectrum*.—The  chemical action of the rays which permeate this glass, are confined exclusively to the central space of the yellow rays. On the first exposure a mere indication of change was the only evidence which was obtained; by allowing the action, however, to continue for a few minutes, taking care that the spectrum still fell upon the same space, a decided olive-brown oval spot .10 in length

was obtained; this was deepened by still prolonged exposure, but not enlarged.

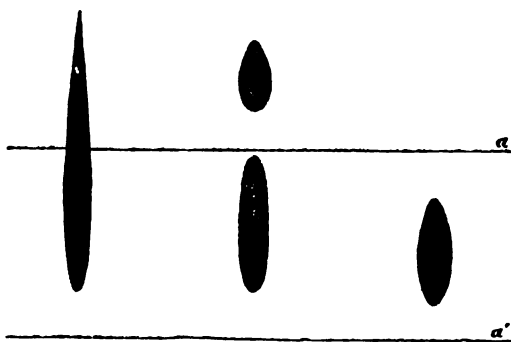
(526.) URANIUM GLASS, *Canary-Yellow*.—This is the peculiar yellow glass which is employed in the manufacture of toilet bottles and other ornamental articles, which transmits a pale yellow light, and disperses an unusual green light. Upon this quality depends its extensive use in ornamental glass manufacture. In my experiments I have employed a slab of this glass, the thickness of which is 1 inch, its width  $2\frac{4}{10}$  inches, and its length  $4\frac{1}{2}$  inches; and independently of some stria, the glass was of a pretty uniform character throughout. This slab enabled me to operate respectively through the several thicknesses of 1, or  $2\frac{4}{10}$ , or  $4\frac{1}{2}$  inches, and thus to determine with very great exactness the thickness of this medium through which the chemical rays would pass. If a block of this glass, which is a canary-yellow when we look through it, is placed upon a piece of black velvet and we look at it, it appears of a fine yellowish-green colour; this green light wanting, however, transparency, and exhibiting more the character of a gleam of monochromatic light piercing through a mist.

If we throw upon the face of this glass a condensed pure spectrum, and look through the sides of it, so as to observe the passage of the rays, its powers of internal dispersion become distinctly visible. From the fixed line *b* we find this dispersion commences, but few of these rays are enabled to penetrate through the 1-inch thickness of the glass. A little above *F* a minimum point is very observable, and from this point the dispersion of the rays becomes very decided; and some of these green rays, when the light is good, penetrate the glass. This green-dispersed light is visible for a considerable distance beyond the ordinary spectrum; the entire space which has usually been designated as the invisible chemical rays, is rendered luminous. [For a more detailed examination of the optical properties of this glass, I must refer to Professor

Stokes's memoir "On the Change of Refrangibility of Light," in the Philosophical Transactions for 1852.]

The ordinary spectrum which permeates this glass is but slightly altered in its character, the condition of the rays after having undergone absorption by this medium being as follows:— Beyond the green ray appears a band of a brownish hue, from the mixture of red with blue; then the blue appears again with considerable brightness. On looking at the coloured fringes produced by the prism, and interposing the uranium glass, it is evident that both blue and violet rays do permeate.

(527.) *Chemical Spectrum*.—The chemical effect produced by the solar spectrum after it has undergone absorption and dispersion by the uranium glass, is not a little remarkable, and requires to be studied with much care. Before each experiment with this glass, it was my practice to obtain an impression from a very pure concentrated spectrum which had not been subjected to any absorption; the object of this being to determine exactly the relation



which the chemical spectrum after absorption and dispersion bore to the unabsorbed image. This was necessary, as it was found there were many variations, from day to day, in the chemical powers of the several spaces corresponding with the coloured rays. Under all circumstances there was the same general character in this impressed spectrum after absorption as in many of those already

described. The action was divided into two well-defined spaces. The rays, which are chemically active from the mean yellow rays up to the blue, produce a well-defined image varying in intensity; first, a dark-olive oval, and above this we have a second, brown oval. This, however, stops short of the end of the visible spectrum, terminating in the mean violet ray. Measurement according to the scale I have adopted throughout, gives the following result. The first image in the figure represents the normal chemical spectrum:—

First indication of chemical action above $a'$	-	-	-	·15
Point of termination of the first oval	„	-	-	·55
Commencement of second oval	„	-	-	·50
Termination of second oval	„	-	-	·90
Entire length of the image formed within the limits of the visible spectrum	-	-	-	·75

A space without any chemical change, equal to ·45, then occurs. This appears to agree with the extreme violet ray and the lavender ray of Sir John Herschel, and the lines of Becquerel and Stokes beyond. Beyond this, that is, at ·45 above  $a'$ , the most refrangible limits of the known spectrum, a third oval forms, the entire length of which is ·40; so that the whole length which undergoes chemical change, is ·115, with the interruption of the action above H to about Mr. Stokes's lines  $l$ . If the spectrum is made to pass through the width of the block of uranium glass, which is  $2\frac{4}{10}$  inches, the action beyond the spectrum is entirely obstructed; but over the space covered by the most luminous rays, chemical action goes on, with an intensity nearly equal to that which is produced when the thickness of the slab about 1 inch only is used for absorption. The third figure in the woodcut represents the result which is obtained after long exposure.

#### QUININE SOLUTION.

(528.) From the interest attached to the peculiar property of the solution of sulphate of quinine in water by

means of dilute sulphuric acid, to bring into view a set of rays beyond the violet, of a beautiful celestial blue colour, corresponding with those produced by the canary-yellow glass, I became anxious to examine the influence of it on the chemical rays. This became the more important, since it had been asserted that the ordinarily dark chemical rays had been rendered visible, and this brought forward as an additional proof of the identity of the rays producing luminous and chemical phenomena.

The solution employed was that recommended by Mr. Stokes, as the best for observing the peculiar phenomena of *fluorescence*, as it has been named, consisting of one part of the sulphate of quinine to 200 parts of water. For the purpose of ascertaining if any greater degree of absorption was produced by using a more concentrated solution than this, experiments were made with such as contained as much as six times this quantity of quinine; but unless this is distinctly stated, solutions of the first-named strength were invariably employed.

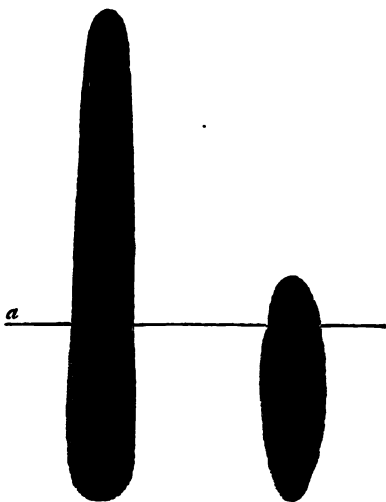
(529.) A plate-glass trough was used; and being first filled with distilled water, the length and general character of the prismatic spectrum was carefully observed and determined. The trough was then filled with the before-mentioned solution of sulphate of quinine, the result of which was sufficiently remarkable. The ordinary rays of the Newtonian spectrum passed the solution freely, and formed a well-defined image upon a screen placed to receive them. According to the strength of the solution employed, so more or less of the violet ray was cut off. The absorptive action on the other rays was quite inappreciable. From the mean violet ray diminishing however, towards the end of the ordinary spectrum, the fluorescent rays penetrate the solution 1 inch in thickness, forming a stream of light of a beautiful celestial blue colour passing across the fluid; beyond this, over a space often nearly equal to the length of the ordinary spectrum, the new rays continue in view, but in no case penetrating

the fluid. Mr. Stokes's observations may be quoted in confirmation of these conditions : —

“In the case of a solution of sulphate of quinine of the strength of one part of the disulphate to 200 parts of acidulated water, it has been already stated that a portion of the rays which are capable of producing dispersed light passed across a thickness of 3 inches. On forming a pure spectrum, the fixed line H was traced about an inch into the fluid. On passing from H towards G, the distance that the incident rays penetrated into the fluid increased with great rapidity, while on passing in the contrary direction it diminished no less rapidly, so that from a point situated at no great distance beyond H to where the light entirely ceased, the dispersion was confined to the immediate neighbourhood of the surface. When the solution was diluted so as to be only one-tenth of the former strength, a conspicuous fixed line, or rather band of sensible breadth, situated in the first group of fixed lines beyond H, was observed to penetrate about an inch into the fluid. On passing onwards from the band above-mentioned in the direction of the more refrangible rays, the distance that the incident rays penetrated into the fluid rapidly decreased, and thus the rapid increase in the absorbing energy of the fluid was brought into view in a part of the spectrum in which, with the stronger solution, it could not be so conveniently made out, inasmuch as the posterior surface of the space from which the dispersed light came, almost confounded itself with the anterior surface of the fluid.”

The mode of operating was the same as that already described, but that the experiments were made with very diffused, and exceedingly concentrated spectra. The object of this was to determine if the less powerful rays were more liable to absorption than those, the energy of which had been exalted by concentration. Hence the various spectra obtained varied in length from 1 inch to 6 inches.

(530.) The annexed woodcut has been copied by the wood engraver with very great care from the actual spectra obtained. [This indeed has been done with all the figures of spectra in this, the quinine series.] The space from  $a'$  to  $a$  was the exact length of the visible ordinary spectrum, and under the conditions of the experiment, *i. e.* a weak sun and a diffused image at a great distance from the slit through which light was admitted, the chemical impression obtained through the trough filled with distilled water was precisely that represented. When the quinine solution was substituted, the second image was the result.

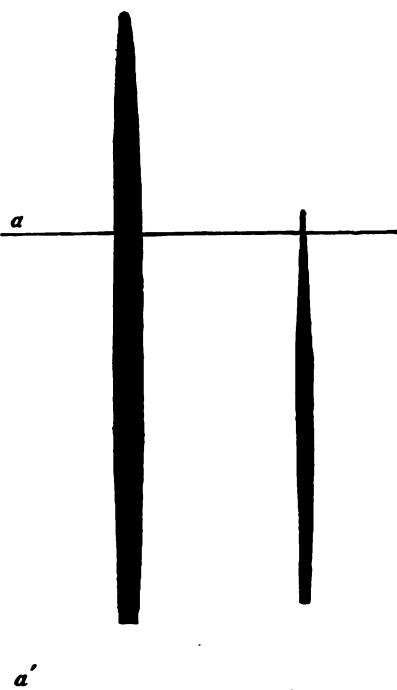


(531.) A weaker solution of the sulphate of quinine  $a'$  was employed, and with a brighter sun than the former, with a less diffused spectrum and longer exposure; the singular elongation of the image down into the orange rays, was the result. My arrangements for keeping the the solar image fixed being imperfect, there was some motion in a horizontal direction, which has given an increased thickness to the impressed spectrum.

(532.) A very intense spectrum was produced by a good achromatic lens, employed in my camera obscura for photographic purposes. The resulting chemical spectrum without the interposition of any absorbed medium was that shown in the annexed figure; the second image being the result of the interposition of the quinine screen, the

exposure in each case being precisely one minute. Upwards of twenty spectra were obtained in the same morning, and, as a constant result, the annexed wood-cut may be regarded as a faithful representation.

(533.) I was anxious to ascertain the relative differences between the spectra obtained on the iodide of silver and those impressed on the bromide. The paper was first washed with a solution of bromide of potassium, 117 grains to six ounces of water; then with nitrate of silver, 170·57 grains to three ounces of water. The spectrum being carefully thrown on the paper by nice adjustment of



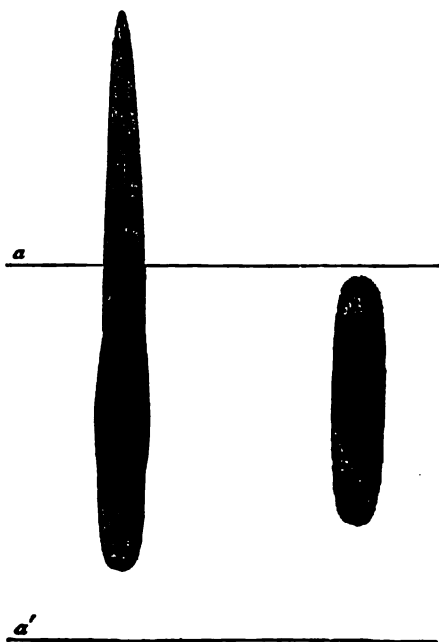
the prism, &c., it was washed with weak gallo-nitrate of silver, the spectrum being shut off by an opaque screen. The screen being removed, the luminous image was allowed to act for one minute, and was then again obstructed. The figure (*next page*) shows the chemical image of the spectrum which had not undergone any absorption, and the second that which was obtained when the quinine trough was interposed.

(534.) It has been repeatedly stated that the rays at the most refrangible end of the luminous spectrum, were rendered chemically inactive by the quinine solution. When bromide of silver is employed, this, as is shown in the figure on the next page, has been sometimes the result; but in no case where the iodide of silver has been employed, has this been found to be the case.



(535.) In conclusion, I may state that, with a view of determining by another method the extent to which the chemical action of the solar radiations were obstructed by the quinine solution and the uranium glass, the following experiments were made:—

My photographic camera was carefully adjusted to embrace a somewhat extensive view, comprehending a granite wall and trees in the foreground, the sea in the middle distance, and a town with an extensive range of hills beyond.



The first view, a very perfect one, was obtained on calotype paper, in fifteen minutes. The glass trough filled with water was then placed in front of the lens, and the paper exposed for the same time as before. The view was not so intense, the radiations from the distant objects and the green leaves of the trees suffering the most by absorption; a very distinct image nevertheless resulted.

The glass trough was filled with the quinine solution. There was very little difference between this and the image obtained when the water was employed, although it was exposed no longer than the others (fifteen minutes). The impression was somewhat redder, and the foliage less perfectly made out; the distant town and land were well made out. The block of uranium (canary-yellow glass) was now interposed, expecting, since through this medium the extra-spectral rays are very active, that an

equally good result with that obtained through the quinine would have been secured. The image obtained in fifteen minutes was very imperfect; it required a considerable time for its development, and the picture eventually was little more than an outline of the objects.

Some peculiarities, which are not easily explainable, are indicated here; for an examination of which I must, however, wait until sunshine and leisure enable me to resume my researches.

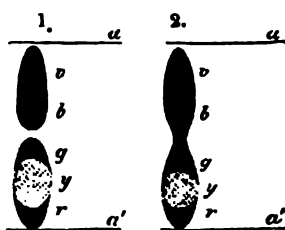
(536.) M. E. Becquerel has stated, "The most refrangible rays are the most absorbable," and "that when any part of the *luminous spectrum* is absorbed or destroyed by any substance whatever, the part of the chemical rays of the same refrangibility is equally so." (*Comptes Rendus*, tom. xvii. p. 883).

The results I have recorded show that this is not a constant result. This, and the peculiarities, *now first observed, of the influence of absorbent media in developing a chemical force in the most luminous rays*, are left for further examination with this passing remark.

### (B.) *Series of Red Glasses.*

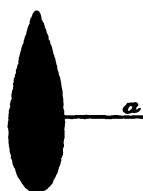
(537.) All the results in the succeeding paragraphs have been obtained upon glass plates with the collodio-iodide of silver.

(538.) VIOLET GLASS.—Rays passed through the glass to the prism. The spectrum appears divided into two distinct parts. The illuminating power of all the rays lessened. In the lower section (1), red, orange, and green are visible; blue and violet occupying the space *b*. If the spectrum is concentrated by a lens and then examined *through* this glass, the images appear as in (2), joined by a thin neck of a neutral tint.



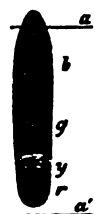
Few spectra are more beautiful than this when all the extraneous light is cut off, each colour being so very distinctly and clearly made out, the diminished illumination enabling the eye to examine it without weariness or confusion.

(539.) *Chemical Spectrum*.—Chemical action commences at  $\cdot 60$  above  $\acute{a}$ , and is then continued with tolerable uniformity to  $1\cdot 35$ , a faint shading being prolonged about  $\cdot 15$  further, or  $\cdot 50$  beyond the luminous spectrum. The long dark oval in the interior of the spectrum exhibits a more intense chemical action than the other portion; this darkened space appears to belong mainly to the upper oval of the luminous spectrum and over the dark space beyond it. In some other experiments, during a period when the sky was covered with light white clouds, and consequently when the intensity of the sunshine was varying, the chemical limits were subject to constant changes, commencing sometimes as high as  $\cdot 70$  and terminating at  $\cdot 30$ .

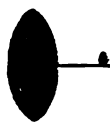


\_\_\_\_\_  $\acute{a}'$

(540.) LILAC GLASS (Manganese).—Reds of flowers seen in strong contrast with the leaves, which appear darker from the loss of their yellow. The yellow rays of the spectrum are nearly obliterated; red shortened; green is gradually lost in black shadow, and all the other rays blended in an intense oval patch of blue.



(541.) *Chemical Spectrum*.—Chemical action commences at  $\cdot 75$  from  $\acute{a}$  and ceases entirely at  $1\cdot 25$ , forming thus one small patch of changed silver, commencing near the line H, and occupying but about one half-inch of space. More than half of the blue rays are inactive, the action being confined to the space of the violet and the lavender rays.

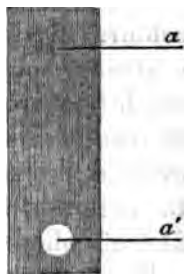


\_\_\_\_\_  $\acute{a}'$

(542.) RED GLASS (Gold).—The spectrum becomes an

oval spot of intense redness with a prolongation of the same colour ; the red oval comprehending all the rays from the upper end of yellow to the end of ordinary red, and the prolongation extends to the edge of the blue.

(543.) *Chemical Spectrum*. — A great number of experiments have been made with the hope of detecting some chemical action on the iodised collodion by the bright crimson rays which permeate this glass. In no instance have I been successful. Instead of obtaining any indication of change, the only result has been the occasional evidence of a protecting action over the spot on which the most intense of the heat rays fall, when diffused radiations have acted on the sensitive surface generally.



(544.) In the second part of the report already referred to, several other experiments are described. The result in all is, however, as nearly as possible, similar to that which is described in the last paragraph.

Not only the glasses coloured with the oxide of gold possess this power of completely stopping the chemical rays ; but those to which the oxide of copper imparts a ruby colour, are equally non-transparent to actinism.

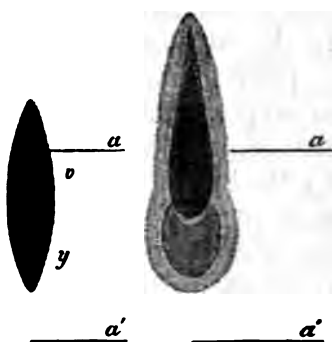
The importance of this to photographers is great, since, with the more sensitive processes, red (ruby) glasses alone are effective in protecting their preparations from change under solar agency. In a room glazed with red glass, the collodion plates do not indicate the slightest degree of change.

#### (C.) *Series of Green Glasses.*

(545.) **APPLE-GREEN GLASS.**—The red rays are shortened one-half, the yellow extends into the orange, and is sharply cut off without any blending at the edge of the red ; on the more refrangible side the green encroaches

considerably on the yellow, and upwards into the blue; the violet by extending into the blue obliterates the indigo.

(546.) *Chemical Spectrum*.—The action appears singularly divided. Two spaces of most intense action speedily appear, corresponding with the green and violet rays as shown at *y, v*, these being surrounded with a band of a chocolate-brown colour. By placing the glass in a strong solution of the hyposulphite of soda the outer band is readily dissolved off, but the ovals *y, v*, resist for a long time the action of the solvent, dissolving, indeed, only when the film of collodion separates from the glass.

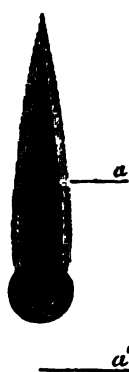


The former result was obtained in *London*. On repeating the experiments at *Falmouth*, a very different effect was produced. The action commencing at  $\cdot 60$ , and continuing to  $1\cdot 60$ , an extended, though much weaker, action is prolonged to  $\cdot 35$ . The experiments having been repeated several times in both localities under precisely the same conditions as regards prism, size of opening between knife-edges, length of spectrum, &c., these results indicate some peculiar atmospheric conditions. This, however, can only be determined by several sets of experiments at widely different periods.

(547.) *INTENSE COPPER-GREEN*.—The spectrum appears as orange, green, blue, and violet. The yellow rays are entirely wanting; a very thin line of red appears at the lower end of orange; the violet is considerably reduced by the loss of red.

In all the deep greens we find the violet rays almost entirely destroyed, owing to the removal of the red. It is from results of this character that I am led to believe the violet rays to be due to a reappearance of red rays amongst the more refrangible ordinary rays.

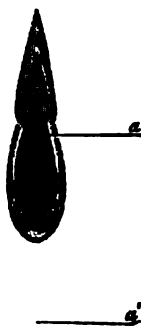
(548.) *Chemical Spectrum*. — Intense action, producing a bronzed line, commences at  $\cdot 60$  and extends to  $1\cdot 10$ , or over a space equal to  $\cdot 50$ . A weak action extends down to  $\cdot 45$ , marking the space occupied by the green ray. A similar modified action extends upward to  $1\cdot 60$ . By long exposure a light fringe appears over the space occupied by the yellow rays, the actual *chemical* spectrum being  $1\cdot 35$  in length. The fringe around the lower part of the spectrum, which is not readily explained, is a tolerably constant result. It may possibly arise from some refraction of the rays near the Fraunhofer line B, within the glass plate.



(549.) *COPPER GREEN of great brilliancy*. — The red below the orange cut off; does not shorten the violet end, but produces a great extension of the blue; the green rays encroach considerably on the yellow. The orange occupies the space of  $\cdot 10$ , the yellow about  $\cdot 16$ , but these rays blending with the green, this is not easy of exact determination; the green occupying a space equal to  $\cdot 25$ , and the blue and violet  $\cdot 38$ . There is a considerable loss of Light in the spectrum.



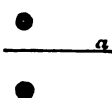
(550.) *Chemical Spectrum*. — Action commences at  $\cdot 60$ , and it is continued with full intensity to  $1\cdot 15$ . This forms a well-defined dark olive green oval spot; it is somewhat smaller at the upper end; the chemical action is then continued faintly to  $1\cdot 35$ , and still more faintly to  $1\cdot 60$ . At the lower end the impressed image descends to  $\cdot 50$ , and a faint border of dusky brown surrounds the spectrum, which is impressed over a space equal to  $1\cdot 5$ . The principal action is limited to the blue and the rays above it.



(551.) **INTENSE GREEN.**—All the rays below the orange are cut off; the yellow and green form one tint of pale pea-green. The blue rays are very light in colour, losing but little of their illuminating power, and these are fringed with a deep band of indigo; no violet rays apparent.



(552.) **Chemical Spectrum.**—The action here on the most sensitive collodion plates is exceedingly slow, and after an exposure of five minutes in the brightest sunshine, the only indication of any chemical action is the appearance of a faint spot near the line H. This when acted on by the pyro-gallic acid becomes very dark, and another spot a little beyond the violet rays makes its appearance.



In the camera obscura, which has been devised for working with the very sensitive and beautiful collodion process in the open air, yellow glasses have been introduced for the purpose, as it was thought, of cutting off the chemical rays, at the same time as Light enough was admitted to enable the operator to see his work. The results obtained clearly prove that rays, chemically active for collodion, pass the yellow media very freely; some green glasses, as the above, offer much more obstruction and were consequently recommended; but more recent experiments have shown that the ruby-red glasses are far more effective than any others.



(553.) **DEEP IRON-GREEN.**—Cuts off the lower red rays; admits the permeation of the orange rays freely. The green very much blended with the yellow, so that it is only by adjusting with great care that a line of yellow can be seen. The blue and violet rays suffer scarcely any change, the lengths of these rays being relatively as follows:—green .30, blue .25, violet .15.



(554.) *Chemical Spectrum*. — The action of this spectrum is very slow, and confined to the limits between the mean green ray and the extreme violet. In a great many experiments the spectrum impressed has been always limited to the space  $\cdot 50$ ; that is, it has commenced in the middle of the luminous spectrum and terminated with the violet rays. Very weak hyposulphite of soda washes off the darkened portion so readily, that I am led to infer that it is an exceedingly superficial dust upon the surface only.

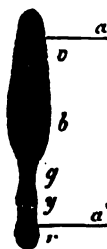
(555.) DEEP IRON-GREEN. No. 2. — All the reds of flowers observed through this glass become nearly black. The spectrum exhibits two spots of pure crimson; perfect blackness between them. A spot of yellow of great purity, from which the green shades off into a light blue, which becomes very bright, and then passes into a line of indigo. The violet is entirely wanting.



(556.) *Chemical Spectrum*. — By long-continued action there is scarcely a trace of any chemical change. Here we have an example of a spectrum in which the blue class of rays, ordinarily called the *chemical* rays, are very brilliant, yet they are chemically inactive upon this most sensitive photographic preparation.

(D.) *Series of Blue Glasses*.

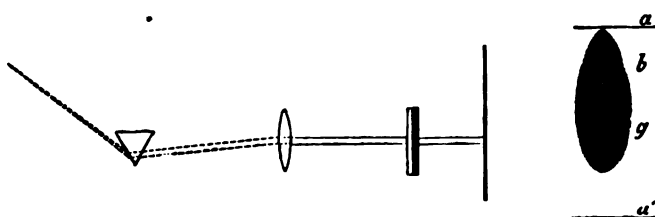
(557.) DEEP COBALT-BLUE. — The red of flowers, as of the Fuchsia, &c., is entirely lost, and not to be distinguished from the green leaves. The surface of leaves appears a grey or blue, with a few exceptions; the *Arbor vitæ* assumes a red-brown colour, remarkable from the striking contrast it makes with the surrounding trees. The leaves of the Currant and several other plants appear red on their under surface when examined through this glass, the light falling on the upper surface, and being transmitted. Yellow Nas-





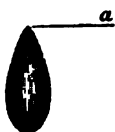


but the red of the violet is entirely removed, forming a



pure blue patch equal to  $\cdot 8$ . Over the space marked *g* the green is far more luminous than over any other part, and the rays gradually darken towards the lower end.

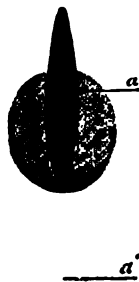
(560.) *Chemical Spectrum*. — The spectrum impressed by long exposure commences at  $\cdot 45$  and terminates sharply at  $1\cdot 0$ , there being no indication of any action beyond the visible spectrum. It will be found by examining the drawing of the luminous spectrum obtained when the Light has passed this combination of glasses, that the action commences at the lower edge of the green rays. The whole space impressed has equal intensity throughout, with a brightening of the silver in the middle.



(561.) A LIGHT BLUE. — The spectrum is represented in its three primary rays, suffering a little reduction in length; when concentrated by a lens a little violet appears at the extreme edge of the blue. Natural objects do not suffer much change when observed through this glass; purple flowers lose more of their red than of their blue, and violet-coloured ones appear nearly pure blue.



(562.) *Chemical Spectrum*. — The action commences at the lower edge of the blue rays  $\cdot 55$  from 0, and extends to  $1\cdot 40$ , when it is suddenly interrupted. Considering the usual character of blue glasses, and that this one is of an unusually transparent nature, it will be necessary to subject it to a much more searching examination than it has yet received. That



the chemical change is very superficial, is proved by the rapidity with which the hyposulphite of soda removes the impression.

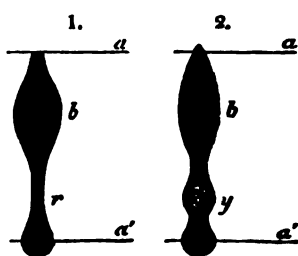
➤ (563.) INTENSE COBALT-BLUE.—

The ordinary red ray disappears, and a pure crimson ray,—the extreme red,—is seen below the lower edge  $a'$  of the ordinary spectrum extending up to the mean yellow.

All the rays but the blue, which

become very intense, and a trace of violet at  $v$ , are obliterated, the red rays being sharply cut off at  $y$ , between which and the blue a dark band appears. When concentrated by a lens, the spectrum is changed, as shown in Fig. 2. The lower crimson ray at  $a'$  becoming a defined circle, surrounded by a band of intense blackness, which extends to the second circle at  $y$ , which, instead of being crimson, as was continued in the neck of Fig. 1, is now of a lavender hue, from the mixture of some yellow with the red, the blue is condensed, the dark space at the lowest edge being an intense indigo.

(564.) *Chemical Spectrum*.—Action commencing at  $\cdot 75$ , extending with full energy to  $1\cdot 50$ ; at the lower edge it is continued with faint shading to  $\cdot 55$ , and even some very slight continuation to  $\cdot 0$ , which is to be detected by placing the collodion glass plate upon a sheet of white paper, viewing it at a small angle, and shading off at the most refrangible end, until at  $2\cdot 10$  all action appears to cease. This is the greatest extension of the spectrum which up to this date (August 20. 1852) has been obtained; and in two experiments made in very intense sunshine at noon-day, a well-marked spot has been obtained  $\cdot 10$  below  $0$ , as marked in the drawing. This spot will be found to cor-



respond with one of Sir John Herschel's heat spots, and may possibly be referred to some peculiar chemical action due to the so-called *parathermic* rays. The presence of vapour, in the form of light cloud or mist, however attenuated, appears to obstruct this peculiar class of rays.

(565.) SMOKE-COLOURED GLASS.—Does not appear to alter the colours of natural objects observed through it. Blue of spectrum nearly obliterated, but the indigo and violet rays are extended; entire length of spectrum is not lessened. The most remarkable feature is the way in which the spectrum is extended over the violet end, proving the existence of red rays far down in the ordinary blue rays.

(566.) *Chemical Spectrum*.—Chemical action commences at  $\cdot 70$  and extends to  $1\cdot 90$ . At the least refrangible end the impression descends faintly to  $\cdot 50$ . The maximum of action is within the limits of the visible most refrangible rays, the most intense spot being near Fraunhofer's line H.

(567.) A much more extensive series of spectra has been obtained, but those examples only have been selected which appear to illustrate general principles. The deductions to be drawn from the above results are numerous and important, but since it is my intention to devote the concluding division of this work to a philosophic examination of the entire subject, the student is referred forward for the views which I entertain relative to both the luminous and actinic spectra.



## CHAPTER XII.

## ON THE POLARISATION OF THE CHEMICAL RAYS.

(568.) IN paragraph 23. of this volume I have given an experiment described by Dr. Young, which appeared to him to prove the analogy of the "visible and the invisible rays." Dr. Young certainly proves in that experiment, that the chemical principle of the sunbeam is subject to the same laws of motion as the luminous principle, since he shows that these rays are capable of producing the phenomena of interference. M. J. E. Bérard, in a paper "Upon the Properties of the different Kind of Rays which are separated by Means of a Prism from Solar Light," which he communicated to the French Institute in 1812, writes: "I received the chemical rays directed into the plane of the meridian, on an unsilvered glass, under an incidence of  $35^{\circ} 6'$ . The rays reflected by the first glass were received upon a second under the same incidence. I found that when this was turned towards the south, the muriate of silver exposed to the invisible rays, which it reflected, was darkened in less than half an hour; whereas, when it was turned towards the west, the muriate of silver exposed in the place where the rays ought to have been reflected, was not darkened, although it was left exposed for two hours." "It is," says Bérard, "consequently, to be presumed, that the chemical rays can undergo double refraction in traversing certain diaphanous bodies; and, lastly, we may say that they enjoy the same physical properties as light in general."

(569.) In a communication to Dr. J. Sutherland of Liverpool, Professor J. Forbes, states: "In spring, 1839,

I tried the experiment of letting the picture formed by polarised Light passing through calc spar to fall upon sensitive paper, then newly discovered: whether from the fault of the paper, I know not, but on my first trial I obtained no kind of effect, and, my attention being occupied with other matters, I never repeated it; but at Birmingham, in August 1839, being requested to give some account of the Daguerréotype which I had seen in Paris, I mentioned the experiment, and pointed out its valuable application to fix with unerring accuracy phenomena of diffraction and polarisation, which different eyes have seen differently, and which, regarded as the test of theories, would thus be preserved with unimpeachable fidelity for examination at leisure by every eye."

(570.) Dr. J. Sutherland of Liverpool, published in the *Philosophical Magazine* for July 1841, a paper on this subject, of much interest and considerable importance. Shortly after the publication of that paper, having the advantage of employing a very excellent solar microscope, with polarising adjustment attached, belonging to a friend, I engaged in precisely a similar set of experiments, and obtained the most satisfactory results. At the time of the publication of the first edition of this work, I attached too little importance to these phenomena of polarisation, and therefore, a mere notice of Dr. Sutherland's experiments and of my own is all that appeared. The advances made in the inquiry demand more exact attention to these phenomena; and since too little notice has been taken of Dr. Sutherland's researches, I am induced to extract some of his observations, and connect them with my own results.

(571.) A prism of calcareous spar was inclosed in a case, with an aperture at one extremity, through which a concentrated pencil of the most refrangible rays of the solar spectrum from a flint-glass prism were passed, producing two well-marked circular images, which fell, in my experiments, upon paper prepared with iodide of silver and

gallic acid. Both images produced some effect, but in nearly all cases—certainly not in all—the extraordinary pencil produced a more decided effect than the ordinary pencil.

(572.) I adopted exactly Dr. Sutherland's arrangement, it is therefore due to him that I copy his description, since I obtained precisely the same result: "An analysing apparatus, consisting of six thin plates of mica, was placed obliquely in the course of the polarised ray, so as to form with its axis an angle of about  $25^{\circ}$ . The instrument was turned round until the plane of the mica plates coincided with the plane of polarisation of the ray. When this was done, the Light was almost extinguished, and was allowed to fall on a piece of photographic paper. After the lapse of five minutes, no effect whatever was produced on the paper. The mica plates were then turned round  $90^{\circ}$ , until their plane was at right angles with the plane of polarisation. The Light was greatly increased in intensity, and in one minute the paper was tinged, in three minutes a good deal so, and in five minutes was pretty dark." When using a second prism of Iceland spar, and transmitting the polarised beam along it, and turning it on its axis until one of the rays was extinguished, a piece of sensitive paper received a dark image from the unextinguished ray, but the extinguished ray produced no effect whatever.

(573.) Having carefully adjusted my apparatus in such a manner that I was enabled to cut off all the rays which have, under ordinary circumstances, any illuminating power, the rays beyond the violet alone were allowed to pass through the Iceland spar. That these *dark rays* did pass was proved by their making two impressions on the prepared surface placed to receive them. The bundle of mica was then employed as before, and in every experiment the result was the same.

(574.) The following result by Dr. Sutherland is instructive. Similar experiments have been recently brought

forward as original, and, let us hope through ignorance of what had been done, Dr. Sutherland's name has not been alluded to.

"I was next desirous of ascertaining whether any phenomena resembling the coloured rings seen round the axes of crystals in polarised Light, were presented by the chemical rays when polarised; and for this purpose I employed an apparatus consisting of a tube two inches long, and three-fourths of an inch in diameter; at one extremity of it was placed a double convex lens, having a focus of one and a quarter inch; within the tube, and at the distance of half an inch from the lens, was placed a section of a calcareous spar rhomb, such as is used for showing the coloured rings. At the other extremity of the tube was placed an oblique analysing bundle of three mica plates, or, one of Nicol's improved prisms, and the apparatus was so disposed that the polarised sunbeam was allowed to fall on the lens, and thence through the tube upon a screen placed close to it. An image of the coloured rings and black cross was thus obtained, and, by turning the tube  $90^\circ$  upon its axis, the rings with the white cross appeared; while in this position a piece of photogenic paper was used to receive the image, and a *reverse impression of the rings and cross was obtained*; to wit, the place where the white cross had been was dark, the centre light, with a complete black ring round it, and segments of other rings exterior to it. The tube was next turned  $90^\circ$  upon its axis, so as to show an image of the rings with the black cross: sensitive paper was again employed, and another reversed impression obtained; to wit, the position of the black cross was white, the centre and inter-spaces dark, with segments of two or three darker circles on them."

(575.) I have frequently determined the polarisation of the chemical rays by reflexion. A Biot's polariscope has been employed for this purpose. The image of the sun, after having been reflected from the mirror, composed of several plates of parallel glass, was thrown on the analysing



plate, the plane of which had previously been turned at right angles to the plane of primitive polarisation, and from this reflected on a piece of calotype paper; in a few minutes an image was obtained, but this was exceedingly faint. The analysing plate was turned  $90^\circ$  upon its axis, and the polarised beam then thrown on the prepared paper, when, almost instantly, a dark impression was made on the paper. These experiments were subject to several modifications, the results in every case, however, proving the polarisation of the chemical rays by reflexion.

(576.) Dr. Sutherland polarised the chemical rays by repeated single refraction, in the following manner. He prepared two bundles of mica plates, nine in each bundle. These were arranged diagonally in a tube, one half of which could be turned round within the other. The tube was turned so that the planes of both bundles were at right angles, and the sun's rays were transmitted through it so as to fall on sensitive paper. In a few minutes little or no effect was produced, but on turning the planes round so as to coincide, an immediate darkening of the paper took place.

(577.) I have constructed an arrangement somewhat similar to this, but using common glass in the place of the mica. The tube containing the polarising bundle was so placed that the sunbeams passed directly through the glass plates to the paper. When the planes were at right angles to each other, the effect, even after prolonged exposure, was weak; but when their planes coincided the paper darkened almost instantaneously.

(578.) By means of a Goddard polariscope and the oxy-hydrogen light, I have obtained very beautiful impressions of the rings of Iceland spar, mitre, quartz, and unannealed glass, upon collodion and Daguerreotype plate and iodised paper.

## CHAPTER XIII.

ON PRODUCING COLOURED PICTURES BY THE SOLAR  
RADIATIONS.

(579.) M. BIOT, in 1840, speaking of Mr. Fox Talbot's calotype pictures, considers as an illusion "the hope to reconcile, not only the intensity, but the tints of the chemical impressions produced by radiations, with the colours of the object from which these radiations emanate." We have produced coloured images—not merely impressions of the rays of the spectrum, but copies—in the camera, of coloured objects, such as geological maps and coloured drawings. As yet these images cannot be fixed with any degree of permanence, but we are advancing rapidly to the desired end.

(580.) It must be remembered that the colour of bodies depends entirely upon the arrangement of the molecules, constituting the first surface upon which the light falls; and that, by either absorption or dispersion, a chromatic effect is produced. We have numerous very beautiful experiments in proof of this. The biniodide of mercury is a fine scarlet when it is precipitated. If this precipitate is heated between plates of glass, it is converted into crystals of a fine sulphur yellow, which remain of that colour if left undisturbed, but which become very speedily scarlet if touched with any pointed instrument. This curious optical phenomenon has been investigated by Mr. Fox Talbot and by Mr. Robert Warrington. Perfectly dry sulphate of copper is white; the slightest moisture turns it blue. Muriate of cobalt is of a pale pink colour; a very

slight heat, by removing a little moisture, changes it to a green. These are a few instances selected from a very extensive class of a similar kind.

(581.) If we receive a prismatic spectrum on some sensitive papers, we have evidence that the molecular or chemical disturbance bears some relation to the colour of each ray, or, in other words, that coloured Light so modifies the action of the chemical principle, that the impression it makes is in proportion to the colour of the Light it accompanies, and hence there results a molecular arrangement capable of reflecting colours differently. In the preceding pages, some instances have been given in which the rays impressed, corresponded with the colours of the luminous rays in a very remarkable manner. One of the most decided cases is that of the paper prepared with the fluoride of soda and nitrate of silver. (196.) Sir John Herschel, was, however, the first to obtain any good specimens of photographically impressed prismatic colourations.

It was noticed by Daguerre that a red house gave a reddish image on his iodised silver plate in the camera obscura; and Mr. Fox Talbot observed, very early in his researches, that the red of a coloured print was copied of a red colour, on paper spread with chloride of silver.

(582.) In 1840 I communicated to Sir John Herschel some very curious results obtained by the use of coloured media, which he did me the honour of publishing in one of his memoirs on the subject, from which I again copy.

A paper prepared by washing with muriate of barytes and nitrate of silver, allowed to darken whilst wet in the sunshine to a chocolate colour, was placed under a frame containing a red, a yellow, a green, and a blue glass. After a week's exposure to diffused Light, it became red under the red glass, a dirty yellow under the yellow glass, a dark green under the green, and a light olive under the blue.

The above paper, washed with a solution of a salt of iodine, is very sensitive to Light, and gives a beautiful picture. A picture thus taken was placed beneath the above four glasses, and another beneath four flat bottles containing coloured fluids. In a few days, under the red glass and fluid, the picture became a dark blue, under the yellow a light blue, under the green it remained unchanged, whilst under the blue it became a rose red, which in about three weeks changed into green. Many other experiments of a similar nature have been tried since that time with like results.

(583.) In the summer of 1843, when engaged in some experiments on papers differently prepared, with a view to test the action of gallic acid on various silver salts I had placed in a camera obscura a paper prepared with the bromide of silver and gallic acid. The field of the camera obscura embraced a picture of a clear blue sky, stucco-fronted houses, and a green field. The paper was accidentally exposed for a longer period than was intended—about fifteen minutes;—a very beautiful picture was impressed, which, when held between the eye and the Light, exhibited a curious order of colours. The sky was of a crimson hue, the houses of a slaty blue, and the green fields of a brick red tint. Surely these results appear to encourage the hope, that we may eventually arrive at a process, by which external nature may be made to impress its images on prepared surfaces, in all the beauty of their native colouration. Such was the language I employed ten years since when the idea of realising this hope was the subject of doubt and even of ridicule; let us now examine what has been effected in this direction.

(584.) Some years since a gentleman, Mr. Hill, of the United States, published in an American Journal the discovery of a process by which colours were fixed on the Daguerriotype plate. Pictures thus naturally coloured were said to have been exhibited, but the public never had, as far as I am aware, any intimation of the process

employed; and it was, in all probability, not so successful as represented, since a long time has elapsed and nothing of the Hillo type has been heard.

(585.) M. Edmond Becquerel was for a long period engaged in experiments connected with this subject; and he appears to have so far succeeded upon silver plates attached by chlorine as to obtain the spectrum in colours, and also impressions of highly-coloured maps, corresponding to the original in colour. I cannot learn, however, that such impressions were ever rendered in any respect permanent; consequently we may regard this result as a slight advance only upon what Herschel had previously done with the chloride of silver.

(586.) M. Niepce de St. Victor has been more successful in obtaining chromatic images than any other experimentalist. I have examined pictures on metallic plates, produced by him, in which every colour of the original was most faithfully represented; these, however, slowly faded out, and became eventually one uniform reddish tint. Niepce has in a memoir, entitled "*Upon the Relation existing between the Colours of certain coloured Flames, with the Heliographic Image coloured by Light,*" drawn attention to some remarkable conditions, which, if confirmed by future experiments, will advance our knowledge of the physical conditions involved in the production of colour.

(587.) The process adopted by this photographer in the preparation of his plate is as follows:—A plate of silver rendered electro-positive, by being connected with a voltaic battery, is plunged into a solution of a metallic or an alkaline chloride, another metal plate being attached to the pole of the battery. The result appears to be the formation of a sub-chloride, which is readily effected by the direct solar rays, and, more slowly, by the weakened radiations in the camera obscura.

(588.) The silver plate is usually, not always, plunged into a bath containing sulphate or chloride of copper, united with chloride of sodium, and by the electro-chemical

action induced a fine brown surface results. This surface, if it is exposed to coloured radiations, suffers a change in direct relation to the illuminating power of the ray ; and hence there results a molecular change, producing a colour of an order corresponding to the colour of the Light.

(589.) M.Niepce, from observing when chloride of sodium (common culinary salt) was used in excess in the bath, that the plate became more susceptible of receiving a yellow colour than any other ; and, remembering that this salt has, in a remarkable degree, the property of imparting a yellow colour to flame, was led to believe some curious relation existed between one phenomenon and the other. These he appears to have investigated with much care, and in the main point, the relation between the colour of the flame and the most decided colour obtained upon the plate, appears to be established.

(590.) The bath is prepared with water holding chlorine in solution, and to this is added the salt, which is essential to give prominence to any particular colour. The salts of strontian are well known for their property of imparting a red, or reddish purple, colour to flame. If a plate of silver connected with the battery is passed into a trough containing chlorine and chloride of strontian, and when thus prepared we place *upon* it a coloured design, we shall perceive, after an exposure for a few minutes to sunshine, that the colours of the image are reproduced upon the plate, but the reds far more decidedly than the others.

(591.) To obtain in brilliancy the other rays of the solar spectrum, other salts are employed.

YELLOWS are obtained by chlorides of uranium, of sodium, or potassium, and by the hypochlorite of soda. Very fine yellows have been obtained, says Niepce, with a bath composed of water slightly acidulated with muriatic acid and a salt of copper.

ORANGE is obtainable by using the chloride of calcium.

GREEN is obtained by using boracic acid, the chloride of nickel, and all the salts of copper.

BLUE and INDIGO are secured when the double chloride of copper and ammonia are in the bath.

RED and VIOLET result from the use in the bath of the chloride of strontian and sulphate of copper. The substances which burn with a white flame, such as the chlorides of lime, lead, and antimony, yield no colour by solar action on the plate.

(592.) All the colours of a picture have been produced by preparing a bath composed of the dento-chloride of copper; and this salt, when thrown into the flame of burning alcohol, produces a variegated flame. Niepce says: — “If we put a salt of copper in liquid chlorine, we obtain a very sensitive surface by a simple immersion in the bath; but the colourific result is rarely good. I prefer a mixture of equal parts of chloride of copper and of chloride of iron, with three or four pints of water; the chloride of iron has the property of receiving on the prepared plates of silver colourific impressions of a similar order to those obtained when copper is employed, and of yielding many colours; but they are much more feeble, and the yellow always predominates. This agrees with the yellow colour produced in flame by this salt.”

(593.) If a bath is formed by uniting with the chlorine water all the substances which give a dominant colour, lively results are obtained. The greatest difficulty arises from our inability to determine the proportions in which the salts should be mixed, one colour frequently obliterating another. Liquid chlorine is necessary; dry chlorine will not produce the same results.—Such is an analysis of the researches of M. Niepce de St. Victor, which are in every respect valuable. To the coloured pictures which he has produced by this method he has given the name of HELIOCHROMES.

## CHAPTER XIV.

GENERAL SUMMARY, AND DEDUCTIONS FROM THE FACTS  
DISCOVERED.

(594.) AT the time (1844) when this work was first published, I felt a strong conviction that, as far as the chemical agency of the solar beam was concerned, the undulatory theory of Light furnished us with no interpretation of the phenomena. The period of ten years which has passed has been, with a few short interruptions only, devoted to the consideration of the question; and I yet feel myself, after many thousands of experiments, the most careful observation of each phenomenon, and the closest possible examination of every section of the subject, unable to surrender my opinion that the theory of vibrations does not explain the action of the solar rays in breaking up the strongest chemical affinities. My views are materially modified, as will be evident, when the reader compares the sequel with what I have formerly written. It is not my intention to discuss the theories of Light with reference to the luminous phenomena of the sunbeam any further than they bear upon the chemical changes to which this volume is devoted.

(595.) In my second chapter I have attempted to give as simply as possible, an "Analysis of the Sunbeam,"—the results of the inquiries of the most eminent natural philosophers, and my own examination. This analysis leads to the conclusion that neither the Newtonian system of seven primary rays, nor that of Brewster, which reduces these to three, can now be received as correct. At the same time we are not in a position to decide the question,



whether the primary rays of Light are three or ten. We know the Newtonian spectrum—that is, the spectrum as known to Newton and described by him—consisted of seven chromatic bands:—*Red, Orange, Yellow, Green, Blue, Indigo* and *Violet*. To these we now add the *Extreme Red* below the Red, and the *Lavender* beyond the Violet. Then we have the sets of rays, which are still of higher refrangibility, appearing in Solution of Leaf-Green as *Red*, in Green Fluor Spar as *Purple*, in Sulphate of Quinine and Decoction of Horse Chesnut Bark as *Blue*, and in the Yellow Uranium Glass as *Green*. These last-mentioned phenomena of colour are referred by Mr. Stokes, — to whose investigations we are deeply indebted for many discoveries in this important branch of physical optics,—to an alteration in the refrangibility of the rays. This view is in perfect accordance with the undulatory theory of Light, in which Mr. Stokes has expressed his firm belief. “To one who regards Light as a subtle and mysterious agent, of which the laws indeed are in a great measure known to us, but respecting the nature of which we are utterly ignorant, the phenomenon (*epipolic dispersion*) might seem merely to make another striking addition to the modes of decomposition with which we are already acquainted. *But in the mind of one who regards the theory of undulation as being for Light what the theory of universal gravitation is for the heavenly bodies*, it was calculated to excite a much more lively interest.” To one, however, who is not wedded to any hypothesis, who has ever desired to wait for an interpretation, rather than render up his mind to imagination,—the view entertained fails to carry conviction. Without rejecting the hypothesis, or substituting another for it, I receive the beautiful series of facts and, examine them in all their bearings on the other phenomena with which more particularly this volume professes to deal.\*

\* “Some enlightened students imagine that the science acquires a satisfactory rationality by being attached to the fundamental laws of universal

(596.) The temperature of these rays has been made the next subject of consideration, and it has been shown that the radiations producing HEAT do not coincide with those producing LIGHT. Their points of maximum effects differ widely, and a remarkable extension of Heat rays has been traced over a large space, where there is no probability we shall ever detect Light. The sensations of these two phenomena are dissimilar—the refrangibility of these radiations are different—the physical effects are in every respect unlike each other, therefore it appears scarcely philosophical to group them together as the results of the same cause. It is, important, however, that their points of resemblance should be noticed.

(597.) A remarkable extension of luminous radiations over a space ordinarily regarded as a dark space has been already noticed, and the question with which we have at

mechanics. The emission doctrine, if it means anything, must suppose luminous phenomena to be in analogy with those of ordinary motion; and if the doctrine of undulation means anything, it means that the phenomena of light and sound are alike in their vibratory agitation, and thus the one party likens optics to barology and the other to acoustics. \* \* \* \* No one doubted the mechanical nature of the principal effects of gravity and sound long before the progress of rational dynamics admitted of their exact analysis. The application powerfully tended to the perfection of barology and acoustics; but this was precisely because there was nothing forced or hypothetical about it. It is otherwise with optics. Notwithstanding all arbitrary suppositions, the phenomena of light will always constitute a category *sui generis* necessarily irreducible to any other: a light will for ever be heterogeneous to a motion or a sound. Again, physiological considerations discredit this confusion of ideas, by the characteristics which distinguish the sense of sight from those of hearing, and of touch and pressure. If we could abolish such distinctions as these by gratuitous hypotheses, there is no saying where we might stop in our wanderings. A chemical philosopher might make a type of the senses of taste and smell, and proceed to explain colours and tones by likening them to flavours and scents. It does not require a wilder imagination to do this, than to issue as a supposition, now become classical, *that sounds and colours are radically alike*. \* \* \* \* Physicists must then abstain from fancifully connecting the phenomena of light and motion.”—AUGUSTE COMTE.

present to deal, is the extent or limits of that influence which, when acting upon the organs of vision enables us to distinguish objects. It is well known that some very remarkable cases of idiochromic vision occur. Dr. Dalton and Mr. Troughton are familiar examples; in their eyes, pure red and pure yellow excited the same sensations. Scarlet and green could not be distinguished from each other.\* In those instances there does not appear to have been any ray of *Light* to which the eye was not sensible; but the power of receiving the impression of colour was wanting. This is a diseased condition of the organ, which bears on the point in question. That is; is it possible we may eventually be enabled to show the existence of Light below the extreme red rays, where heat rays are detected? It will be found, that if several persons, who are looking at the same prismatic spectrum, are requested to mark with the point of a needle the limits of the coloured rays, not many of them will mark the same spot; some see more of the violet or of the red rays than others, and consequently will point a little higher or lower as the case may be. Now, if we protect the eye from the luminous rays by a piece of cobalt-blue glass, we are enabled to see a class of rays that are less refrangible than the ordinary red, and which have been called "the extreme red rays." Sir John Herschel first pointed out the means by which a "*lavender grey*," ray may be shown to exist beyond the violet. If, indeed, the spectrum is received upon paper, dyed with an alcoholic tincture of turmeric, the spectrum appears elongated beyond the violet ray; but the eye is affected with the sensation of a pale yellow colour. A paper dyed with an alcoholic tincture of the dark purple dahlia, alkalised with carbonate of soda, which becomes in about twenty-four hours a fine yellow colour, exhibits this pro-

\* Dr. George Wilson, of Edinburgh, is engaged in the investigation of the phenomena of colour-blindness, and we may expect much valuable information from his researches.

longation as a pale yellow streak. "If such," says Sir John Herschel, "should be the true calorific character of these rays, we might almost be led to believe (from the evident reappearance of redness, mingled with blue in the violet rays) in a repetition of the primary tints in their order, beyond the Newtonian spectrum; and that if by any concentration rays still further advanced in the 'chemical' spectrum could be made to affect the eye with a sense of light and colour, that colour would be green, blue, &c., according to the augmented refrangibility." Something like this is actually the case, as Mr. Stokes's discoveries have shown.

(598.) It has been supposed that some animals may have the power of distinguishing such colours, that is that their eyes are affected by those rays of high refrangibility, which produce no impression of *Light* upon the eyes of man. M. Biot has, it would appear, found that some such effect is produced upon the eyes of some of the night-roving animals, by rays invisible to us. This may be. That which is *darkness* to us when we come from the sunshine into it, is found after a little time, when the lenticular arrangement of the eye has been adjusted to the required condition, to produce the sensation of tolerable *Light*. May we not, therefore, explain on the same principle, the power which the cat, the owl, and other animals possess of seeing in the circumstances we might regard as darkness? This reasoning is not calculated to settle the question, whether the eyes of any animals receive sensations of *Light* from the rays of heat, or of those producing chemical change; and it does appear that a broad distinction is established between the solar influence, Heat, and the solar influence, *Light*. That in many phenomena their operations so run together, that it is impossible to separate the one from the other, I am ready to admit. The experiments of Delaroche have been interpreted as showing that *Light* and *Heat* are convertible into one another. The curious fact, discovered by

this philosopher, that radiating heat becomes more and more capable of penetrating glass as the temperature increases, till at a certain temperature the rays become luminous; almost seem to confirm this, did they stand alone. The results obtained by Melloni with the solar rays do, as it appears to me, contrary to his own arguments, compel us to consider Light and Heat as two distinct powers, intimately connected with each other in their operations.

(599.) It is now necessary to examine with great care the question of the identity or otherwise of the chemical principle ACTINISM, which we derive from the same solar source. It must have been remarked, that one of the most striking peculiarities which the prismatic spectrum presents, in its action on sensitive preparations, is the remarkable difference between the scale of action on preparations, not very dissimilar from each other. This is shown in the frontispiece, and reference to it will render it unnecessary to do more than allude to two or three remarkable examples.

(600.) The limits of solar action upon twenty-nine different preparations: mineral and vegetable, is shown in the Plate. The maximum will be found,—marked by the dotted line,—to vary in every instance, but with the exception of three salts of gold (12. 15. and 18.), and the juice of the ten weeks' stock (27.), it will be seen that these maxima are confined within the limits of the least refrangible blue, and the most refrangible violet rays. No. 1. Nitrate of silver shows that the action ceases a little beyond the visible spectrum, and that the rays of the yellow space have but little action; and that those of the red are confined to very small limits. No. 4. Iodide of silver and ferro-prussiate of potash, exhibits the influence of a chemical force to a great distance beyond the luminous spectrum at the violet end. The same influence greatly modified in power is exerted again over the space covered by the red, and extra-spectral calorific rays; and

No. 5., which is a specimen of the action of the hydriodic salts upon the darkened chloride of silver, shows the extension of a purely chemical action considerably lower in the calorific region; and this is even still further extended in No. 22., ferro-cyanate of potash, and per-chloride of iron. In all, but No. 18., the strongest impression is made by the chemical agency of those rays within the limits of the luminous spectrum; but in this remarkable instance, the action is confined entirely to the non-luminous space beyond the violet rays. In No. 14., chloride of gold, this action is entirely confined to the region of the blue, indigo, and violet rays, whilst No. 16., the proto-cyanide of gold, and formobenzoate of silver; the influence is extended with great force to a considerable distance beyond the violet rays, and a large amount of chemical power is exerted by the rays found in the region of the red space. These, and the other instances, which are described in their proper places, sufficiently show, that the action is extended over the entire luminous spectrum, and spaces occupied by dark rays, nearly equal to twice the length of the visible spectral image. A singular difference is also exhibited in the action of the different spaces on different materials.\* In those preparations only which are obtained from the vegetable kingdom do we detect any action over the spaces covered by the yellow rays; the point of maximum illuminating effect.

(601.) By the investigations to which the art of photography has given rise, we have discovered, that the chemical influence is not confined to the class of blue rays, and the dark rays beyond them, as was formerly thought. This chemical power has been traced over every ray of the luminous spectrum, and to some distance beyond its least refracted end, as well as the end of most refrangibility. It is also found that the maximum point, although it may be said to lie within the limits of the most refrangible

\* See Appendix.—Becquerel's Experiments.

rays for nearly all preparations ; yet, that is not found at the same point for any two, however slight the difference between them may be.

(602.) Melloni has endeavoured to explain this. The hypothesis which this philosopher has given, supposes all bodies to have, what he terms "a chemical colouration." To render his meaning clear, we must diverge from our subject slightly. If we paint a board, of the seven prismatic colours — or take, which is still better, seven pieces of cloth of the same colours as the rays ; and receive the spectrum upon them, we shall find when all the rays fall upon their own colour that the colour of each is considerably exalted. If we receive the spectral image upon a red ground, all the rays will suffer diminution in intensity, except the red, which will be increased. If, on the contrary, it is received on a blue ground, the blue ray will become more intense, whereas all the others will, in different degrees, be diminished. Melloni, therefore, reasoning by analogy from these differently reflective powers of various colours, supposes all bodies, even a white sheet of paper, to have an invisible "chemical colouration ;" and hence as the colour of the body presented to the spectrum belongs to that of one or other of the rays, so is the maximum chemical power of that ray exalted, whilst all the others are depressed. We find that coloured media allow the passage of a larger quantity of the rays of their own particular colour than of any other. We also find that colourless fluids admit the permeation of the chemical influences of the solar beam in very different degrees. Hence M. Melloni argues, that according to the "chemical colouration" of the fluid, so is its permeability to the different rays which produce chemical change. This is certainly an exceedingly ingenious hypothesis, and we may by it explain a great number of phenomena ; but it appears to me an unnecessary refinement in speculative philosophy, to build so elaborate and complicated a structure upon a foundation so purely imaginary. Any speculation from

so eminent a philosopher as Melloni, to whose researches on Heat we are indebted for the elucidation of some of the most complicated phenomena of this element, must be received with all the respect due to the efforts of an original mind; but at the same time we must not be led too widely astray by an entire reliance upon authority. It would appear that M. Moser has borrowed his ideas of the colours of the "latent Light" of vapours from this philosopher.

(603.) It is necessary for the fair and full consideration of the question, that the views of another experimental philosopher should be examined—those of the younger Becquerel. I shall, therefore, extract a few passages from the translation of E. Becquerel's Memoir on the Constitution of the Solar Spectrum in the *Scientific Memoirs*, Part XII. August, 1843.\* "It has been generally admitted that these radiations which accompany Light are different from each other, and that according to such or such a sensible substance, the active rays were also different; but I do not suppose that the question is so complex. In fact, the luminous phenomena, according to the theory of undulations, depend on the vibrations of the molecules of the illuminating body, which are transmitted to the retina by the intermediation of the ether, the molecules of which are themselves in vibration. Fresnel, whose beautiful investigations have contributed to the triumph of this theory, had stated that the chemical effects produced by the influence of Light, are owing to a mechanical action exerted by the molecules of ether on the atoms of bodies, so as to cause them to assume new states of equilibrium, dependent on the nature and on the velocity of the vibrations to which they are subjected. This idea had been suggested to him by a remarkable experiment of M. Arago, the result of which was to show, that the chemical

\* See also *Annales de Chimie*, November, 1843, for an extended memoir by the same author, and Appendix.



rays which influence the chloride of silver, interfere in the same manner as the luminous rays. (See Frontispiece, last figure.) I think that the hypothesis of Fresnel is accurate, and even that it may be extended further, especially if we consider that the chemical and phosphorogenic rays possess the same physical properties as the luminous rays; thus they are subjected to the physical laws of reflection, of double refraction, of polarisation, and of interference, in the same manner as are these rays; and, moreover, the spectra of these different radiations have the same lines. Thus, it would be more simple to suppose —

“1st. That a pencil of solar rays is the union of an infinite number of rays of different refrangibility, each ray arising from undulations of ether, not having the same velocity.

“2dly. That, by refracting a pencil of solar rays through a prism, we have the solar spectrum, which possesses different properties, on account of its different action on external bodies.

“3dly. That, with respect to certain substances, the molecules of which are united by weak affinities, such as salts of silver, of gold, of mercury, &c.; the solar rays act according to the velocities of undulation, which may be transmitted to the molecules of matter, and consequently between certain limits of refrangibility. I have called the whole of the rays which affect a substance a *chemical spectrum*.

“4thly. That phosphorescent bodies becoming luminous by means of the molecular movement impressed on their molecules, a movement which gives rise to the separation of the two electricities, necessary for maintaining the molecular equilibrium, and the neutralisation of which forms the flashes we observe, we may consider the action of the solar rays on these bodies, as analogous to that of these rays on bodies chemically sensible, with this difference only, that the mechanical action of the molecules of

ether is transmitted to these bodies without chemical decomposition. According to their nature, therefore, these phosphorescent substances are sensible between certain limits of refrangibility, in the solar spectrum.

"5thly. Besides, if we consider the retina as an organ which perceives the vibrations of the ether, it is only sensible to rays contained between certain limits of refrangibility, and the active rays form a spectrum, which in this case, is found to be the luminous spectrum.

"According to this hypothesis, we shall bring back all the effects produced under the influence of Light, to the action of one same radiation upon different bodies, and there will be as many spectra, as there are sensible substances. This mode of viewing the subject is verified on all the phosphorescent bodies, and on those whose molecular state changes under the action of the solar rays. As to the luminous rays, or those which act upon the retina, we can only judge of them by our own sensations; but it is probable, that the retina of the different beings which exist on the surface of the globe, are not all sensible between the same limits of refrangibility. We have some examples of this; amongst others of fish which live in the depths of the sea; and which see how to find their way which would not be perceptible by our organs."

(604.) This last assumption is purely gratuitous, we know perfectly well, that as we descend in the ocean zone after zone in depth, the colour of fishes gradually and regularly declines, and they degenerate in their order of organisation. That at the depth of about fifty fathoms around our own shores, all vegetable life ceases, and that in the clearest seas and that under the brightest skies all animal life is extinct at three hundred fathoms from the surface, consequently no fishes exist in spaces dark to the human eye.

(605.) Much stress has been laid upon the fixed lines of the chemical spectrum, as proving the identity of the actinic with the luminous force. In the frontispiece will

be seen the fixed lines obtained by M. E. Becquerel upon a Daguerréotype plate, and those of Mr. Stokes' fluorescent rays are described, page 49., par. 63. M. Arago, it appears, first suggested to M. E. Becquerel a set of inquiries, connected with the action of the rays of the spectrum on the same body placed in different media, say *air* and *water*. It was not found that any difference was produced by either of these media. The fixed lines were the same in each, although the velocity of Light is much quicker in water than in air. On this M. Arago remarks:—"The velocity with which a luminous ray *passes through* a given body, depends exclusively on the refringency of this body, and on the *velocity of emission of the ray*, on the velocity it had *in vacuo*. The ray which reached the surface of the stratum of iodine through the water at the point where it meets this surface, possesses a velocity superior to that which the ray that moved through the air had at the same point; but in the interior of the stratum, at a sufficient depth, the two rays possess exactly the same velocity. Let us make the photogenic phenomena depend not upon an action exerted at the surface, but upon an action originating in the interior of the stratum, and every difficulty disappears; only—a single result—we are compelled to establish an essential distinction between the interior and the surface of a stratum, the thickness of which is incredibly small."

(606.) All this is so purely hypothetical that it scarcely requires a remark. We know that the action always commences on the very surface of the sensitive film. We know that the chemical action is retarded by water,—that of Light, according to the undulatory view, is quickened. Indeed, Arago himself subsequently wrote:—"It is by no means proved that the photogenic modifications of sensitive substances result from the action of solar Light itself. These modifications are perhaps engendered by invisible radiations, mixed with Light, properly so called, proceeding with it and being similarly refracted. In this case the experiment

would prove, not only that the spectrum formed by these invisible rays is continuous, that there are solutions of continuity as in the visible spectrum, but also that in the two superposed spectra these solutions exactly correspond."

(607.) Reference back to the chapter, which treats of the influence of absorptive media upon the chemical action of the solar rays, will be necessary in the consideration of the connection between Light and actinism. The following paragraphs, to (603.), are preserved as they were written in 1841.

(608.) If we pass the sunbeams through a deep yellow glass, or, which is still better, a solution of the sulphate of chromium, we rob them of but very little of their Light or Heat; but it will be found that they are deprived of the greatest part of their chemical influence. Sensitive papers may be exposed behind such a glass or such a fluid for a considerable length of time without undergoing any change.

(609.) An instance of the intense power of pale yellow media is the following:—DALTON's solution of quadro-sulphuret of lime, prepared by boiling lime and sulphur in plenty of water, scarcely seems to impair the brightness of white objects seen through it in thicknesses of an inch or two.

The spectral image, passed through such a fluid, exhibited but small apparent loss of illuminative power; "*but its total photographic effect must have been diminished, by the loss of at least four-fifths of its amount.*" (Herschel.)

(610.) A coloured atmosphere acts in the same manner. The case mentioned by Sir John Herschel in his Memoir "On the Chemical Action of the Rays of the Solar Spectrum," which I will quote, is to the point:—"It is probable that other atmospheric relations than those which refer to the extinction of the merely luminous rays are concerned in this phenomenon. The tint of coal smoke is yellow (as may be seen in perfection in a London November fog), and more than one instance of the *intense*

*power* and capricious singularities of very pale yellow media in their action on the *chemical rays* will come hereafter under our notice. In the locality from which this paper is dated (Slough), a light easterly wind brings with it abundant smoky haze from London, to which rural prejudices assign the name of 'blight,' and attribute an insect origin. *On such occasions, when the sky has been otherwise cloudless, I have been continually at once annoyed and surprised by the slowness of photographic action, and by the fugitive nature of its results under the process of fixing."*

(611.) The power which chlorine gas, diluted with common air, has of absorbing this chemical principle is very great. Although so pale a yellow is the mixture, it does not appear that there is any actual loss of Light, by the interposition of a vessel thus filled, over that which would occur with a bottle of common air: it will be found that the influence producing chemical change is absorbed in a remarkable manner, and photographic preparations of the most sensitive kinds, change with the utmost slowness, behind even this pale yellow gaseous medium.

(612.) At the Cork meeting of the British Association a paper from Dr. Draper was read, detailing the following experiment, which is interesting:—Within a very large vessel, filled with a mixture of chlorine and hydrogen, was placed a small one filled with the same gaseous mixture; and this arrangement was exposed to the sunshine. Of course the gases in the outer vessel speedily combined, and the vessel was filled with the vapour of muriatic acid; but the gases in the interior vessel, although Dr. Draper has shown that an exceedingly small influence will occasion them to combine, were found to be unaffected. The atmosphere surrounding this inner vessel had, although allowing the passage of a flood of Light, separated the chemical principle, which alone had the power of inducing the combination.

(613.) It has been observed by Daguerre, and almost by every photographer since the announcement of his

discovery, that the sun two hours after it has passed the meridian, is much less effective in the photographic processes, than it is two hours previously to its having reached that point. May not this depend upon an absorptive power of the air, which we may reasonably suppose to be more charged with vapour two hours after, than two hours before, noon?

(614.) If we take a considerable thickness of a dense purple fluid, as, for instance, a solution of the ammonia-sulphate of copper, we shall find that the quantity of Light is considerably diminished — at least four-fifths of the luminous rays are absorbed; but the so-called “chemical rays” permeate it with the greatest facility, and sensitive preparations are affected by this influence, notwithstanding the deficiency of Light, nearly as powerfully as if exposed to the undecomposed sunbeams. Those deep blue glasses which are coloured with cobalt, and which are commonly used for finger glasses, have nearly the same effect of obstructing LIGHT, but allowing the free passage of this principle which accompanies it.

(615.) In the valuable paper to which I have already several times referred, Sir John Herschel mentions the curious property of the muriate of chromium, “which reduces the spectrum to two narrow and pretty well defined spaces, coloured the one red and the other green, the red being that of the extremity of the spectrum, and the green of great purity and richness of tint.” On photographic papers this analysed spectrum impresses two circular spots, whose centres coincide with those coloured images exactly in the green, and nearly so in the red: one spot is intensely black, and the other white. The same authority has also proved that a preparation of the colouring matter archil—the rocellate of potash—admits the permeation of a great quantity of green light; “such as, had its properties not been altered by the medium it had traversed, could not have failed in the time the exposure lasted to have produced a considerable blackening

of the paper," which was however unchanged over the green luminous spaces. These experiments are very illustrative: they show the existence of a chemical principle in the region, but at the same time quite independent of the colour of the ray.

(616.) If we examine the photographic images impressed by the spectrum itself, as represented in the plate, or any other series, it will be seen that the luminous rays



occupy but a very small space compared with the influences of heat and chemical power. If the linear measure, or the diameter of a circle which shall include the luminous rays, is 25, that of the calorific spectrum will be 42.10, and of the chemical spectrum 55.10. Such a series of circles may well be used to represent a beam from the sun, which may be regarded as an atom of *Light* surrounded with an invisible atmosphere of *Heat*, and another still more extended, which possesses the remarkable property of producing chemical and molecular change.

(617.) We may regard the centre or maximum of this

power as situated somewhere about the most refrangible blue or the lower edge of the indigo ray, the shifting of this point, as we vary the materials, preventing us from fixing the spot with precision. Towards the most refrangible end of the spectrum we find, as might be expected, the power slowly diminishing in force with the most perfect regularity, until at a certain point, even the *most sensitive* preparations can detect no chemical action. On the contrary, as we approach the most luminous rays, the action is abruptly stopped, the light-giving power has interfered with the chemical power, and in a great many cases all action ceases at this point. In some others this point, where the effect of Light is the greatest, having been past, the chemical power is again exerted, and a similar interference is, in some cases, strikingly shown by the maximum calorific rays, although we have abundant evidence of a chemical principle extending far into that invisible region of the spectrum.

(618.) The action of the red rays of the prismatic spectrum, which it is now important we should consider, has invited the examination of a great number of experimentalists; and some varied, and apparently opposing, results appear to have been obtained. In 1839 Sir J. Herschel first pointed out that the least refrangible rays of the spectrum exerted a protecting action upon several photographic preparations. Subsequently M. Edmond Becquerel was led to believe that the red, orange, and yellow rays had the power of continuing the action which had been commenced by the more refrangible rays. He therefore divided the rays of the spectrum into two sets, giving to the rays existing at the blue end of the spectrum the name of *exciting rays* and to those at the red end the name of *continuing rays*. M. Gaudin, shortly after the publication of Becquerel's Memoir, stated that, having placed a Daguerrréotype plate in the camera obscura, and allowed the lenticular image to act upon it for a time quite insufficient for the development of any visible image,—



he placed it beneath a yellow glass,—he succeeded in producing a complete development of the image without the application of mercurial vapour.

(619.) Upon the Daguerréotype plate and upon the ordinary photographic papers a dissimilar action is constantly exerted by the rays at the two extreme ends of the spectrum. On the light-coloured salts of silver on paper, the rays above the green darken, while for a considerable time those below the green protect the paper from change. That is, they not merely do not blacken themselves, but they retard, and in many cases entirely check, the action of rays which do produce that chemical change which is indicated by darkening the white surface. The effects upon the Daguerréotype plate are similar to those. It has been stated that if the papers or plates are affected by the chemical radiations of the blue end of the spectrum, and then brought under the influence of the red end, that the action is continued, as Becquerel's and Gaudin's Experiments appear to show. This is not constantly the case, indeed it is doubtful if the actions are the same in any instance. Mr. Wilson, in 1776, stated that the most refrangible rays excited phosphorescence in the sulphuret of lime, *but the less refrangible ones extinguish it when shining*. Ritter found that chloride of silver, darkened in the violet rays, had its colour partially restored by the red rays. Wollaston showed a similar result in the action of the spectrum on guaiacum; and this has been confirmed by Sir John Herschel. I have shown, that if we wash a paper covered with darkened chloride of silver with a solution of iodide of potassium, and expose it to the action of the spectrum, that portion covered by the blue, violet, and extra-spectral rays is whitened, while that upon which the yellow and red rays fall is very rapidly blackened.

(620.) The Daguerréotype picture is, as is well known, developed by the agency of mercury (167.). The iodide, bromo-iodide, or whatever preparation of silver may be employed, is decomposed by the action of the chemical

radiations, and the mercury attacks the portions of the plate over which this change has taken place, and always in proportion to the amount of change. The moment chemical change commences, the *dormant* picture is formed, and it has been shown by M. Claudet that the effect is almost instantaneous. As iodine is liberated it attacks the surface of the plate immediately beneath the film which has first undergone a change; and this is continued, until eventually the plate is blackened, or *solarised*, as the technical expression is. As in the case of the chloride on paper darkened by exposure to the most refrangible rays, which loses colour under the action of the red rays, so a darkened Daguerreotype is considerably lightened by exposure under a monochromatic red glass. Now, M. Gaudin's image does not appear to be produced by a class of rays which can strictly bear the name of the *continuing* rays. The action by which an image yet dormant on the silver plate is evoked by the rays which belong particularly to the Heat and Light spectrum, appears to belong to the physical phenomena described under the general head of thermography. The iodide of silver has suffered that disturbance by which the chemical affinities are loosened. Then, by covering the plate with a yellow or a red medium, more especially the latter, the Heat or Light rays—sometimes both—separate the particles more directly from each other, the iodine is no longer held by surface (epipolic) force, and from the arrangement of the finely divided silver the picture results. These examples, and several others which have been noticed, all lead to the conviction that these peculiarities are merely the balance of action between the three forces of the sunbeam—LIGHT, HEAT, and ACTINISM.

(621.) As it regards the *continuing* action of M. Becquerel, we find that a prolonged exposure of the plate to the spectrum does not produce the result. Dr. Draper first observed this, and I have repeatedly verified his results:—“I found that it was perfectly immaterial

whether the exposure to the spectrum was for thirty seconds or one hour, the result was the same. The final action had been produced, the less refrangible rays had carried their region (the part of the plate on which they fell) to the unaffected state, while the more refrangible had solarised theirs. Now, if the phenomenon was due, as M. E. Becquerel supposes, to an unequal action of the same kind in different rays, it is obvious that the final result ought to depend on the time of exposure; the red ray, aided by daylight, should carry its portion through the various shades of white, and solarise it at last. But this, in the longest exposure, never takes place; that part of the plate remains as though a ray of light had never fallen upon it."

(622.) We have some curious examples of the protecting actions alluded to. M. Claudet endeavours to take an impression of the sun, when seen as a red globe through a mist. The Daguerriotype plate is sensibly affected by the diffused daylight over every part, but where the sun's image falls there is not a trace of an image. The solar rays in this example protect the plate from the influence of the diffused daylight which is sufficiently active to produce a chemical change over every other part of the sensitive surface.

(623.) Herschel noticed an extended action of this kind on the tartrate of silver, and about the same time I observed it on a Daguerriotype plate. In these examples the protected space was extended around the spectrum, and observable even above the violet. Some experiments and remarks by M. Claudet and Dr. Draper are of much importance. Mr. Claudet was puzzled with some apparent contradictions in the results obtained; at one time he finds red and yellow Light continuing the action, and at another time destroying it. M. Claudet then remarks:—

(624.) "I have again examined my former experiments, and I find some specimens which show that red and yellow glasses have destroyed the effect of the photogenic Light on plates simply iodised. How can this fact be reconciled

with Messrs. Ed. Becquerel and Gaudin's experiments, and those I had just made in consequence of these philosophers' observations? Had I made any mistake in the classification of my former specimens, or had I erred in my mode of operating? This might be, and I feared such was the case, as I just obtained quite different results. I then questioned my assistant, and he recollected well that we had repeatedly experimented upon plates simply iodised, and that we had then found that red and yellow glasses did destroy the action of daylight, as well on iodised plates as on those which had been submitted to the compound vapour of iodine and bromine.

"I then recollected a curious fact mentioned by Dr. Draper of New York, which at the time of its publication I had found so inexplicable that I did not pay much attention to it, and which I had totally forgotten during the course of my experiments.

"Dr. Draper said:—'Such are the facts I observed, and they seem to have been reproduced by MM. Foucault and Fizeau; but there are also others of a much more singular nature. In these Virginia specimens *the same protecting action reappears beyond the violet.*

"'The only impressions in which I have ever seen this protecting action beyond the violet, are those made in Virginia in 1842; they were made in the month of July. Struck with this peculiarity, on my return to New York the following August I made many attempts to obtain similar specimens, but in no instance could the extra-violet protecting action be traced, though the analogous action of the red, orange, yellow, green and blue, was perfectly given. Supposing, therefore, that the difference must be due either to impurities in the iodine or to differences in the method of conducting the experiment, I tried it again and again in every possible way. *To my surprise I soon found that the negative effect was gradually disappearing;* and on Sept. 29. it could no longer be traced, except at the highest part corresponding to the yellow and green rays. In December it had become still more imperfect, but on

the 19th of the following March the red and orange rays *had recovered their original protective power*. It seemed, therefore, that in the early part of the year a protective action had made its appearance in the red ray, and about July extended over all the less refrangible regions, and as the year went on it had retreated upwards.

“‘Are there, then, periodic changes in the nature of the sun’s light?’ &c.

(625.) “From these experiments of Dr. Draper it would appear that, according to the months of the year in which we operate, the red and yellow rays either do or do not exercise a destructive action. It must be remarked that Dr. Draper mentions only iodised plates, that he always speaks of iodine alone, and that he never alludes to bromine or chlorine, which were hardly in use at the time of his experiments.

“Dr. Draper adds:—‘I further found, that when different rays are brought to act upon each other, the result does not alone depend upon their intrinsic differences, but also on their relative intensities. Thus the green and lower half of the blue rays, when of a certain intensity, protect the plate from the action of the daylight; but if of a less intensity, they aid the daylight.

“‘The red and orange rays, when of a certain intensity, increase the action of daylight on the plate; but if of a less intensity, they restrain it.’

“It would result from this last observation of Dr. Draper, that when the red and orange rays are not endowed with the destructive action, they, on the contrary, have the property of continuing or assisting the action of day light.

“Is it not, then, possible, that, like Dr. Draper, I may have made my first experiments on the iodised plate during the period when the red and yellow rays were endowed with their destructive action, and that Messrs. Becquerel and Gaudin may have made theirs when these rays had lost their destructive, and had acquired their continuing action, at a period corresponding to the present?

“ Having made my experiments with the greatest care, I seize with satisfaction this manner of explaining phenomena apparently contradictory. It would, indeed, be curious and interesting to find that neither myself nor the other experimenters are in error, and that we differ only as regards conditions and circumstances, which, without our knowledge, have exercised an influence upon our experiments. But there can be no doubt as regards the iodised plate, when it has been subsequently submitted to the vapour of bromine alone, or of bromine and chlorine united. I have operated with these substances during the various periods of the year, and I have invariably found that the red, orange, and yellow glasses destroy the action of daylight.”

(626.) On the influence of atmospheric changes the following remarks are of importance:—

“ The possible simultaneous existence of two antagonistic lights reflected from the atmosphere explains those anomalies which are so annoying to photographers; for example, those circumstances under which it seems impossible to obtain any image, whatever may be the length of exposure in the camera. This difficulty is imputed to the preparation of the plates, the state of the accelerating solutions, &c.; and after all it only exists in the light. As much effect is often obtained in 30 seconds as in 120 seconds, for it is possible to have obtained a first effect which has been afterwards destroyed; and that must inevitably be the case if, during the latter part of the exposure in the camera obscura, any clouds or vapours have suddenly rendered the light of the sun yellow; in this case the object which had first reflected white light, becoming capable of reflecting only yellow light, this last must destroy the effect produced by the first.

“ If the object reflects at the same time blue light from the zenith and yellow light from the southern horizon, the two lights may be neutralised and destroy each other, so that no photogenic effect can be obtained. Sometimes,

when the sky is cloudless, the space at the zenith is of a particularly deep blue colour; whereas the vapours produced by the heat of the sun make the sky appear slightly tinted with yellow, from the horizon to a certain height. In those circumstances all photographers must have observed that the operation in the camera obscura is excessively slow.


(627.) "This may probably explain those dark specimens, which were so weak in effect, obtained some years ago on the Alps during clear and cloudless weather, by an operator sent to Italy by M. Lerebours to take Daguerreotype views. M. Lerebours' operator was an experienced photographer, and he found, to his great surprise, that on the summit of the Alps he could not obtain any effect in less than five or six times what he considered to be the necessary exposure. He was surrounded with snow, the sun was shining in all its brilliancy, the sky was pure and cloudless, of a deep blue colour, whereas the horizon was without doubt slightly tinted yellow, on account of the vapours produced by the melting of the snow and ice of the glaciers.

"Mr. Lerebours' operator was using at that time (in 1840) plates only iodised; and this fact would confirm the neutralisation of the photogenic effect upon plates of iodide of silver, by the less refrangible rays acting simultaneously with white light, according to Dr. Draper's observations.

"It would be interesting if M. Lerebours could state the period of the year in which his artist operated on the Alps; although it might be that from the high elevation of those regions the operator was precisely in those atmospheric conditions which exist on less elevated grounds during only certain months, on account of the density of the atmosphere that the sun's rays have to penetrate."

(628.) When M. Arago made his "Report on the Daguerreotype," before the Chamber of Deputies in 1839, he used these words:—"Upon examining several of the pictures to be submitted for your inspection, all will con-

sider the immense advantages which would have been derived, during the expedition to Egypt for example, of a means of reproduction, so exact and so rapid ; all will be struck with this reflection that, if photography had been known in 1798, we should this day have possessed faithful representations of many valuable antiquities now, through the cupidity of the Arabs and the vandalism of certain travellers, lost for ever to the learned world." Now, this hope was long before it was entirely fulfilled. It was of course imagined that, under the brilliant sun and clear skies of the south, photographic pictures would be produced with much greater quickness than they could be in the atmosphere of Paris. It was found, however, that with the original Daguerreotype plate a much longer time was required. Even in the clear and beautiful light of the higher Alps, it has been proved that the production of a photographic picture requires many minutes more, even with the most sensitive preparations, than it does in London. It has also been found that, under the influence of the brilliant light of Mexico, twenty minutes, and half an hour, were required to produce effects, which in England would occupy but a minute ; and travellers engaged in copying the antiquities of Yutacan have on several occasions abandoned the use of the photographic camera, and taken to their sketch-books. Dr. Draper has observed a similar difference between the chemical action of the Light in New York and in Virginia. This can only be explained on the supposition that the intensity of the Light and Heat of those climes interferes with the action of the actinic rays on the sensitive preparations which were employed. Dr. Draper furnished a prismatic image, impressed upon a Daguerreotype plate in Virginia, which exhibited many remarkable peculiarities : it has been described in a previous chapter. Nothing could be more valuable than a series of such pictures of the spectrum, produced in different degrees of latitude, and at different elevations. It would be very easy to procure





them from our magnetic observatories in different parts of the world, and these would afford much valuable information on this point. Where an organic compound is combined with the silver salt employed, the sensibility is so quickened that chemical changes take place under the most intense Light and Heat of tropical climes.

(629.) These numerous facts group themselves together thus:—

LIGHT is white, colourless, until it comes in contact with matter. It then suffers variable degrees of decomposition, by reflection, refraction, dispersion, and unequal absorption, and the result is colour. Rays of a particular colour are found to occupy, in a marked manner, particular divisions of the spectrum. Red occupying the lower edge, or the least refracted portion, while rays of the blue class occupy the other extremity, or the limits of greatest refraction.

HEAT, in its radiant state, produces no sensation of colour, it occasions the separation of the particles of matter from each other, and by the encreasing bulk of the mercury in a thermometer tube, or by the drying of a volatile fluid, we determine the fact, that LIGHT and HEAT do not obey the same laws of refraction. The maximum of HEAT being found below the red rays, that of LIGHT, considerably above them in the yellow rays.

ACTINISM, produces none of the phenomena of Light or Heat. It is much more refrangible than either. Where Light and Heat exist in their greatest force actinism cannot exert its power; therefore, on all the preparations of gold, silver, &c., the spaces covered by the yellow and the red rays produce no effect, but the maximum of chemical change is found to exist where there is least Light, and scarcely a trace of Heat.

(630.) It has been stated that every ray has a definite amount of chemical action, and that by obstructing that ray we obstruct the chemical action, that they are in fact inseparable. Reference to the experiments detailed will

show that such is not the fact. The blue ray, to quote one example, has freely passed a coloured transparent medium, and yet been entirely deprived of chemical power. It has been obliterated and the chemical power has remained unchanged.

(631.) Again, the peculiar fluorescent phenomenon of the spectrum has been spoken of as the chemical rays rendered luminous—made visible; yet, by a block of uranium glass we stop back the fluorescent rays, and allow the permeation of rays which are chemically active. Beyond this, it appears, that we have the power of developing chemical action in the yellow rays, where it was previously masked, by the use of the same medium.

(632.) LIGHT, in its pure condition, as *light*, capable of being decomposed into the primary rays, will not produce chemical change.

The great exceptions to this are:—organic compounds, which, it has been shown, will change under the influence of Light, separated as far as we possibly can separate it from the chemical principle,—and vital organisms, which appear to require the peculiar excitement due to the luminous principle of the solar rays for the support of that great living principle to which growth belongs. No chemical compound of any of the inorganic elements has yet been discovered upon which *pure Light* produces a chemical change.

HEAT, as a radiant force, in some cases does effect a change, but it is of an essentially different character from that produced by actinism. On these grounds, therefore, I still hold to my belief, that the chemical power of the sunbeam, ACTINISM, is a physical agent widely different from LIGHT or HEAT, but associated with these principles in their modes of motion.



## A P P E N D I X.

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### No. I.

#### HIMLY'S METHOD OF PREPARING THE PROTO- AND PER-CYANIDES OF POTASSIUM AND GOLD.

[*Referred to from page 148.*]

THE *Protocyanide of Potassium and Gold* is best obtained by dissolving seven parts of pure gold in nitro-muriatic acid, precipitating with excess of ammonia, washing the fulminating gold that is formed, and then putting it into a hot solution of six parts of the cyanide of potassium in water. The liquid is decolorised and ammonia disengaged. From the concentrated solution the double salt crystallizes in beautiful prisms.

The *Percyanide of Potassium and Gold* is very easily obtained when thirty-five parts of gold are converted into chloride of gold, as neutral as possible, and the aqueous solution of that salt is united gradually with a hot solution of forty-six parts of cyanide of potassium. The liquid loses colour, and on cooling of the concentrated solution, the double salt separates, in large prisms, which, on exposure to the air, or in vacuum, become milk white, giving off their water of crystallization.

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### No. II.

#### ON SOME EARLY EXPERIMENTS IN PHOTOGRAPHY, BEING THE SUBSTANCE OF A LETTER ADDRESSED TO ROBERT HUNT, ESQ., BY THE REV. J. B. READE, M.A., F.R.S.

(*Referred to from Introduction.*)

Stone Vicarage, Aylesbury,  
February 13. 1854.

MY DEAR SIR,—In giving you the information you require respecting my early researches in photography in 1836 and following years, I may assume that you are already aware, from my letter to Mr. Brayley of March 9, 1839, and published in the "British Review" for August, 1847, that the principal agents I employed, before Mr. Talbot's processes were known, were infusion of galls as an accelerator, and hyposulphite of soda as a fixer.

I have no doubt, though I have not a distinct recollection of the fact, that I was led to use the infusion of galls from my knowledge of the early experiments by Wedgwood. I was aware that he found *leather* more sensitive than *paper*; and it is highly probable that the tanning process, which might cause the silver solution to be more readily acted upon when applied to the leather, suggested my application of the tanning solution to paper.

In your own history of the photographic process, you say "the discovery of the extraordinary property of the gallic acid in increasing the sensibility of the iodide of silver was the most valuable of the numerous contributions which Mr. Talbot has made to the photographic art." It is nevertheless true, as stated by Sir David Brewster, that "the first public use of the infusion of nut-galls, which is an *essential element* in Mr. Talbot's patented process, is due to Mr. Reade," and in my letter to Mr. Brayley I attribute the sensitiveness of my process to the formation of a gallate or tannate of silver. I need scarcely say, that among various experiments I tried gallic and tannic acid in their pure state, both separately and mixed; but the colour of the pictures thus obtained with the solar microscope was at that time less pleasing to my eye than the rich warm tone which the same acids produced when in their natural connexion with solutions of vegetable matter in the gall-nut. This organic combination, however, was more effective with the solar microscope than with the camera, though the lenses of my camera were five inches in diameter. It is probable enough that the richer tone was due to the greater energy of direct solar rays. In using the solar microscope, I employed a combination of lenses which produced a convergence of the luminous and photogenic rays, together with a dispersion of the calorific rays, and the consequent absence of all sensible heat enabled me to use Ross's cemented powers, and to make drawings of objects inclosed in Canada balsam, and of living animalcules in single drops of water. The method I employed was communicated to the Royal Society in December, 1836, and a notice of it is contained in the "Abstracts."

You inform me that some persons doubt whether I really obtain *gallate of silver* when using an infusion of gall-nuts, and that one of Mr. Talbot's friends raises the question. It is sufficient to reply, that though gallic acid is largely formed by a long exposure of an infusion of gall-nuts to the atmosphere, as first proposed by Scheele, yet this acid does exist in the gall-nut in its natural state, and in a sufficient quantity to form gallate of silver as a photogenic agent; for M. Deyeux observes, that "when heat is very slowly applied to powdered gall-nuts, gallic acid sublimes from them, a part of which, when the process is conducted with great care, appears in the form of small white crystals." M. Fiedler also obtained gallic acid by mixing together a solution of gall-nuts and pure alumina, which latter combines with the tannin and leaves the gallic acid free in the solution; and this solution is found, on experiment, to produce very admirable pictures. But what is more to the point, Mr. Brayley, in explaining my process in his lectures, showed experimentally how gallate of silver was formed, and confirmed my view of the sensitiveness of the preparation. It is therefore certain that the use of gallate of silver as a photogenic agent had been made public in two lectures by Mr. Brayley at least two years before Mr. Talbot's patent was sealed.

I employed hyposulphite of soda as a fixer. Mr. Hodgson, an able practical chemist at Apothecaries' Hall, assisted me in the preparation of this salt, which at that time was probably not to be found, as an article of sale, in any chemist's shop in London. Sir John Herschel had previously announced the peculiar action of this preparation of soda on salts of silver, but I believe that I was the first to use it in the processes of photography. I also used iodide of potassium, as appears from my

letter, as a fixer, and I employed it as well to form iodide of lead on glazed cards as an accelerator. Iodide of lead has of itself, as I form it, considerable photographic properties, and receives very fair impressions of plants, lace, and drawings when placed upon it, but with the addition of nitrate of silver and the infusion of galls, the operation is perfect and instantaneous. Pictures thus taken were exhibited at the Royal Society before Mr. Talbot proposed his iodized paper. The microscopic photographs exhibited at Lord Northampton's in 1839 remained in his lordship's possession. I subsequently made drawings of sections of teeth; and one of them, a longitudinal section of a tooth of the *Lamna*, was copied on zinc by Mr. Lens Aldous for Owen's "Odontography." I may say this much as to my own approximation to an art, which has deservedly, and by universal consent, obtained the name of Talbotype.

Sir David Brewster, in his "History of Photography," passes immediately from the experiments of Wedgwood to those of Talbot; but the "Transactions of the Royal Society," to which my friend Mr. Gravatt has directed my attention, will enable us to insert, if not a chapter, at least a very pregnant parenthesis. The Bakerian Lecture, in 1803, by Dr. Young, who never touched a subject without leaving his mark upon it, contains a highly interesting and original experiment on the photographic representation of the invisible chemical rays beyond the blue end of the spectrum. This experiment does not happen to be recorded in the first edition of your "Researches on Light;" but no one will refer to it with greater pleasure than yourself, not only because it is the first photographic analysis of the spectrum, but also because it has the higher merit, even as it stands alone, of being the one sufficient fact which establishes the consummation so devoutly looked for, at the conclusion of your work, from the persevering accumulation of facts only; for it is in itself a simple and demonstrative proof, to use the words of Dr. Young, of the general law of interference, and, in your own words, "reconciles the chemical action of the photographic force, *energias*, with the undulatory theory of *light*." Dr. Young's experiment forms the conclusion of his lecture, and is given in the following terms:—"The existence of solar rays accompanying light more refrangible than the violet rays, and cognisable by their chemical effects, was first ascertained by Mr. Ritter; but Dr. Wollaston made the same experiments a very short time afterwards, without having been informed what had been done on the Continent. These rays appear to extend beyond the violet rays of the prismatic spectrum, through a space nearly equal to that which is occupied by the violet. In order to complete the comparison of their properties with those of visible light, I was desirous of examining the effect of their reflection from a thin plate of air capable of producing the well-known rings of colours. For this purpose I formed an image of the rings, by means of the solar microscope, with the apparatus which I have described in the Journals of the Royal Institution, and I threw this image on paper dipped in a solution of nitrate of silver, placed at a distance of about nine inches from the microscope. In the course of an hour, portions of three dark rings were very distinctly visible, much smaller than the brightest rings of the coloured image, and coinciding very nearly in their dimensions with the rings of violet light that appeared upon the interposition of violet glass. I thought the dark rings were a little smaller than the violet rings, but the difference was not suffi-

ciently great to be accurately ascertained; it might be as much as  $\frac{1}{30}$ th or  $\frac{1}{40}$ th of the diameters, but not greater. It is the less surprising that the difference should be so small, as the dimensions of the coloured rings do not by any means vary at the violet end of the spectrum so rapidly as at the red end. For performing this experiment with very great accuracy a heliostate would be necessary, since the motion of the sun causes a slight change in the place of the image; and *leather impregnated with muriate of silver* would indicate the effect with greater delicacy. The experiment, however, in its present state is sufficient to complete the analogy of the invisible with the visible rays, and to show that they are equally liable to the general law (of interference), which is the principal subject of this paper."

It detracts nothing from the greatness of Dr. Young to say, that although the philosophy of this experiment is permanent truth, yet the spectral image of it soon faded away. Photography was not then, at the beginning of the century, an art as permanent as it is elegant and useful. Little was wanted to make it so, but it hung fire for nearly fifty years, till Talbot supplied that little.

I have just learnt from Admiral Smyth, that his friend Dr. Peacock, the Dean of Ely, has for the last seven years been engaged on a *Life of Dr. Young*; and when the work appears, we shall have a more accurate knowledge of the man who was unquestionably the Newton of his day. Like his illustrious predecessor, he was a pioneer in the philosophy of light; and, as we have seen, by a single photographic experiment, overlooked hitherto by us all, has shown a perfect analogy between the undulations of the visible and invisible rays. Had he happened to head his chapter, as Wedgwood does, "On a Method of taking Pictures by the Agency of Light on Nitrate of Silver," his name and place would have been duly marked; but because theory, and not experiment, was the great point before him, the philosophical photographer is overlooked by the practical one.

Dr. Young's propositions are, that radiant light consists in undulations of the luminiferous æther, that light differs from heat only in the frequency of its undulations, that undulations less frequent than those of light produce heat, and that undulations more frequent than those of light produce chemical and photographic action,—all proved by experiments.

You close your own "Researches on Light" by proposing the following questions as of the greatest importance for future investigation:—"Is *energia* absorbed by material bodies? Does it influence their internal constitution? Is it radiated from bodies in the dark, or at all concerned in the production of any of those changes which have been attributed to *dark rays*?"

Dr. Young's hypothesis seems to anticipate your questions, and almost to answer them in their order. He says, "All material bodies have an attraction for the *ætherial medium*,—by means of which it is accumulated within their substance,—and for a small space around them—in a state of greater density, but not of greater elasticity." (Bakerian Lecture, 1801.) Hence he considers material bodies to have within them latent light, latent heat, and latent chemical force, or "*energia*" (which is, in his opinion, a particular condition of the *ætherial medium*); that the luminous, calorific, and chemical phenomena are exhibited under two

modifications,—the vibratory or permanent, and the undulatory or transient state; and that the forces which produce these several effects differ from each other only in the frequency of their undulations or vibrations.

Such are the conclusions at which the all-inquiring Dr. Young arrived in 1801, on a subject which in 1850 is proposed for our investigation. Well may Admiral Smyth say, "How strange it is that we are still but half-acquainted with the results of his powerful mind!"

Of course I shall not quarrel with you if you do not accept his conclusions, *totidem verbis*; because, as I am aware, you see reasons for believing that light, or that agent which affects the organs of sight, is broadly distinguished from those rays which bring heat from its solar source, and both of these classes form those which produce, in the constitution of bodies, those singular changes which are more particularly the objects of your study. But Sir John Herschel has shown that, by certain artifices, even the extreme rays may be rendered visible; and Dr. Young, by an experiment most ingenious, and to his own mind, at least, most conclusive, has demonstrated the analogy of the invisible with the visible rays. I feel sure, therefore, that while adducing and discussing the proofs of your own theory, you will be glad to take the opportunity afforded by your second edition of placing Dr. Young's name in the niche which Fame has left empty.

Believe me to be, my dear Sir,

Very truly yours,

To Robert Hunt, Esq.

J. B. READE.

### No. III.

(Referred to from Preface and page 225.)

#### ON THE USE OF BLUE GLASS IN ACCELERATING GERMINATION.

Edinburgh, 1. George the Fourth's Bridge,  
September 8, 1853.

MY DEAR SIR,—I am favoured with yours of the 5th, relative to my practical experience in the effect of the chemical agency of coloured media on the germination of seeds and the growth of plants.

I must first explain that it is our practice to test the germinating powers of all seeds which come into our warehouses before we send them out for sale; and, of course, it is an object to discover, with as little delay as possible, the extent that the vital principle is active, as the value comes to be depreciated in the ratio it is found to be dormant. For instance, if we sow 100 seeds of any sort, and the whole germinate, the seed will be the highest current value; but if only 90 germinate, its value is 10 per cent. less; if 80, then its value falls 20 per cent.

I merely give this detail to show the practical value of this test, and the influence it exerts on the fluctuation of prices.

Our usual plan formerly was to sow the seeds to be tested in a hot-bed or frame, and then watch the progress, and note the results. It was



usually from eight to fourteen days before we were in a condition to decide on the commercial value of the seed under trial.

My attention was, however, directed to your excellent work, "On the Physical Phenomena of Nature," about five years ago, and I resolved to put your theory to a practical test. I accordingly had a case made, the sides of which were formed of glass coloured blue or indigo, which case I attached to a small gas-stove for engendering heat; in the case shelves were fixed in the inside, on which were placed small pots wherein the seeds to be tested were sown.

The results were all that could be looked for: the seeds freely germinated in from two to five days only, instead of from eight to fourteen days as before.

I have not carried our experiments beyond the germination of seeds, so that I cannot afford practical information as to the effect of other rays on the after culture of plants.

I have, however, made some trials with the yellow ray in preventing the germination of seeds, which have been successful; and I have always found the violet ray prejudicial to the growth of the plant after germination. I remain,

My dear Sir,

Very faithfully yours,

To Robert Hunt, Esq., Hull.

CHARLES LAWSON.

#### NO. IV.

#### ON THE GLASS IN THE PALM HOUSE OF THE ROYAL GARDENS AT KEW.

(*Referred to from Preface.*)

December 6. 1845.

SIR,—I am directed by Lord Lincoln to refer to you the accompanying papers relative to the proposed introduction of coloured glass into our new Palm House at Kew, and I am requested that they may be referred to Mr. Hunt, for the benefit of his well-considered opinion, in the shape of a report.

[Signed]

T. S. PHILLIPS.

*Sir Henry De la Beche.*

Royal Gardens, Kew.  
Nov. 23. 1845.

MY DEAR SIR,—The more I think and inquire upon the subject of coloured glass for the Palm Stove, the more I am struck with its importance, especially as connected with so vast a concern as we are erecting. White glass does occasionally scorch the foliage of the plants. Stained or coloured glass does act upon vegetation, as has been clearly ascertained by Mr. Hunt, in his ingenious experiments; a gentleman, I under-

stand, in one of the departments of the Woods and Forests—the Economic Museum. May I be pardoned, then, if I return the enclosed unreported upon, and take the liberty of suggesting that Mr. Hunt be consulted on this important question. Dr. Lindley would not give an opinion, and he said that Mr. Hunt was the only person in the Kingdom competent to do so. Mr. Hunt, however, should know that it is not with deeply coloured glass that we have to do, but just so much stained (if staining will have the effect) as will deprive the glass of its *scorching* character, and not affect the vegetation. The tint most recommended is a faint purple. \* \* \* \*

[Signed] W. J. HOOKER.

Edinburgh, 15th November, 1845.

SIR, — I beg leave to take the liberty of just mentioning I arrived here to-day from Haddon House, where I am erecting additional works for the Earl of Aberdeen, who has kindly said he would be happy to recommend me to the English ministers of the Continent of any capital I may wish to visit; and as I hope (D. V.) to be in London next week, with a view of going to Antwerp, and possibly to Bohemia, in pursuit of a very superior coloured glass, the *violet* tinge; or azure hue, which I understand will be a wonderful improvement for the Royal Palm House and Inner Circle Winter Garden, and, indeed, all horticultural structures, as it beautifully softens the light, and hinders the rays of bright sunshine destroying as much as it does when transmitted through the clear glass, which is found to scorch and wither the tender foliage, as they first appear, and subsequently the blossoms, except they are most carefully blinded by some artificial means. As I am most solicitously anxious to be the first to introduce this desideratum in conservatories, and more particularly in those two I feel myself so very highly honoured to erect—at Kew and Regent's Park—and being of such immense magnitude, the improvement would be so immense, as well to render them additionally enjoyable to visit and walk in as for the plants, &c., &c.

[Signed] RICHARD TURNER.

*Alexander Milnes, Esq.*

*Memorandum respecting the Coloured Glass most favourable for Glazing a Hot or Greenhouse.*

THE consideration of the question as to the applicability of coloured glass to horticultural purposes resolves itself into two or three particular points to which it is necessary every attention should be given.

In the first place, we have to consider the conditions required for healthful vegetation. In the second, to examine how far these conditions are met by the use of media which will transmit certain classes of the solar rays to the abstraction of others; and if coloured glasses admit the

permeation of rays of their own colour. Thirdly, to inquire into the conditions required for the Palm House at Kew.

1. The result of my experiments, continued over some years, is to prove that the chemical rays of the solar spectrum, which are represented in the greatest power by the blue, indigo and violet rays, are the most active in producing the germination of seeds, and assisting the young plant up to the perfect development of its first leaves. After this period these rays become too exciting, producing the same effect on plants as pure oxygen gas would on animals. They induce rapid growth, and the leaves of the plant assume a healthful colour; but the perfect development of its parts is prevented, and the flowering and fruit-bearing processes are checked, in many cases destroyed, the plant perishing rapidly after a certain period of its growth. Under the isolated influence of the luminous rays, represented by the orange and yellow rays, seeds will not germinate. But, after germination has taken place, and the plumule formed under the chemical or blue rays, I have found that the luminous or yellow rays are not injurious.

Indeed, experiments appear to prove they are more adapted for producing woody fibre than any other class of rays. The following results, the average of many experiments, will show this—

Plants growing under the influence of blue rays left of carbon				7.16 per cent.
Ditto	"	"	red rays	- " - 7.25 "
Ditto	"	"	green rays	- " - 7.60 "
Ditto	"	"	yellow	- " - 7.69 "

The effect of the red or calorific rays is to produce rapid evaporation from the soil and the surface of the plants; even when this evaporation is met by an increased supply of moisture, germination is much retarded, and the young plant grows slowly, its leaves assuming a brown or red tint, showing that the chlorophyl—the colouring matter of healthy leaves—is prevented from forming.

The green rays may be regarded as preserving a position between the luminous and the chemical rays; and under certain conditions, into which it is not now necessary to enter, they produce very favourable results upon plants. It will be seen that these peculiar actions of the dissevered rays bear directly upon the conditions of plants during the spring, summer, and autumnal seasons; and the conditions of the solar radiations during these periods afford satisfactory evidence in support of the correctness of the experiments named. In the spring, the luminous and thermic power of the sun-rays is less than their chemical influence. Germination and all the processes of a new growth are excited. In the summer, light and heat, increasing, act as interfering agents; the chemical excitation is subdued, and the processes of the formation of woody fibre are in full activity. The ripening of grain and fruits, depending more upon the calorific rays, ensues with the autumn, when the luminous effects and certainly the chemical powers of the solar forces are lessened.

2. It being impossible to keep the isolated prismatic rays for any prolonged period, or in sufficient quantity for satisfactory experiment in action upon plants, recourse was had to various transparent media—glass and coloured fluids held in glass cells. In most cases, I gave the preference to coloured fluids in my own experiments, as they allowed of my

adjusting their tints to any point of the chromatic scale. At the same time I used coloured glasses extensively, and with care I have been enabled to procure well-insulated rays in tolerable purity.

But it must be distinctly understood that the colour of any medium is not to be regarded as representing the colour of the rays by which it is permeated.

Cobalt-blue glass admits, besides the blue class of rays, the passage of the green, and a large portion of the red rays. Deep-red glasses may be permeated by yellow and blue rays, and yellow glasses are freely passed by blue and red rays, beyond the orange and yellow class. It will, therefore, be necessary that any kind of glass selected for a particular purpose should be examined as to the relation it bears to the coloured rays of the solar spectrum. If this is not attended to, the result may be very different from that anticipated.

3. It is required, according to Sir W. Hooker's letter of the 23rd of November, that a glass should be selected for the Palm House at Kew, "*so much stained as will deprive the glass of its scorching character and not affect the vegetation.*" Two conditions are here required to be met. One, the production of a glass which shall obstruct the more intense thermic rays, and the other a glass which shall not affect the vegetation.

One only of these conditions is complied with in the use of glasses of a "faint purple," as suggested by Sir W. Hooker, or of the "violet tinge or azure hue" recommended by Mr. Turner. Any of these colours would, by obstructing light, give an increased action to the chemical principle of the sun-beam, and consequently excite an unnatural growth in the palms.

If a *green glass* of the proper tint is selected, all the conditions are complied with. The experiments of M. Melloni first proved the influence of green colour in obstructing the free permeation of radiant heat through transparent bodies. My own experiments, in particular reference to the growth of plants, have in the fullest degree confirmed this.

Green glass coloured with oxide of copper to a tint which may be called a pea-green will admit light and chemical power in the same proportions as white glass, but it will obstruct the passage of those rays which produce the "*scorching*" desired to be avoided. I, therefore, should recommend for the Palm House, considering the probable conditions of the solar radiations over the countries—Italy, Sicily, and Barbary, to which the palm is indigenous—the use of a medium for glazing it, which would not interfere with the light or chemical power of the sun's rays, but which would obstruct a particular class of heating rays; namely, a tested green glass.

For the germination of seeds, the striking of cuttings, &c., a green or a hot-house glazed with a pure blue glass would be desirable, and also for the cultivation of alpine plants\*, which are more exposed in nature to the action of the unabsorbed chemical radiations from an intense blue sky. Our object in all cases appears to be to endeavour to imitate, not to force the conditions of nature.

ROBERT HUNT.

*Sir Henry De la Beche.*

\* I have been led to doubt the correctness of this part of my recommendation since that time.

Museum of Economic Geology,  
6th December, 1845.

MY LORD,—Having referred the consideration of the kind of coloured glass desirable to be employed in the Kew Palm House, to Mr. Hunt, in conformity with your Lordship's directions, I have the honour herewith to transmit his report on the subject.

[Signed]

H. T. DE LA BECHE

*The Rt. Hon. The Earl of Lincoln.*

Office of Woods, &c.,  
9 July, 1846.

SIR,—Adverting to the report which you made in December of last year, in reply to the reference as to the kind of coloured glass desirable to be employed in glazing the New Palm House in the Royal Botanic Gardens at Kew, I am, in behalf of the Commissioners of Her Majesty's Woods, &c., to acquaint you, that as the time has now arrived for deciding as to the description of glass to be adopted, the Board, agreeably to your recommendation, desire to adopt a glass coloured with oxide of copper, to the tint commonly called pea-green; but as the adjustment of the tint may be of great importance, and involve some nicety in matters of which they consider you are particularly competent to judge, the Board have directed Mr. Decimus Burton, the architect of the building, and Mr. Turner, the contractor for the works, to place themselves in communication with you, so that under your instructions a specimen may be procured to your satisfaction; and I have therefore to request the favour of your assistance in the course of proceeding the Board purposes to adopt.

I am, sir, &c.,

[Signed]

A. MILNE.

*Robert Hunt, Esq.*

Museum of Economic Geology,  
December 16, 1846.

MY LORD AND GENTLEMEN,—Agreeably to the request of Mr. Milne, as conveyed in his letter of the 9th July, I placed myself in communication with Mr. Decimus Burton, and Mr. Turner, on the subject of the tinted glass, which the Board, on the recommendation of my memorandum of the 6th December, 1845, appears desirous of adopting in the new Palm House at Kew.

I have been supplied by these gentlemen with thirty-seven specimens of green glass, the whole of which I have submitted to an experimental examination, the purpose of which was to ascertain the relative amount of obstruction which they offered to the passage of the solar-heat rays, which Sir William Hooker, in his letter of the 23rd November, 1845, says "scorches the foliage of the plants."

I found in these examinations, which consisted of measuring off the various thicknesses of the coloured bands of the prismatic spectrum, and of experiments on their chemical and thermic action, after they had permeated these variously tinted green media, that it was quite within my power to cut

off nearly the whole of the sun's heating rays, without obstructing much of the light. Experiments in which I have been engaged for some years, prove that one class of the sun's rays materially quicken vegetation ; and that under their influence plants might be excited into unnatural growth ; whilst to another class a restraining power belongs, by which this stimulating principle is modified, and under their united influences the healthful growth of the plant is secured. It therefore became important to discover a medium which should not disturb the natural proportions of these classes of rays, the unequal permeation of which would be injurious to the palms, but which should at the same time prevent that intense action of the heat rays, which is already complained of, and which in the new Palm House would, in all probability, be much more energetic, owing to its form. Another point which I felt it necessary to regard with particular attention, was the general appearance of so large and so ornamental a structure as that which is now being built in the Royal Botanic Garden. I have the satisfaction of being enabled to report that I have selected a glass which, from its peculiar composition, secures the required condition for the plants, and which is so slightly tinted, as to present no appearance by either reflected or transmitted light materially different from the white sheet glass already employed for glazing the stove house for the orchideous plants at Kew ; and which is more transparent than much of the crown glass in the old houses in these gardens.

This glass admits most freely the permeation of all the luminous and chemical rays, and obstructs only those heat rays which are remarkable for their peculiar scorching power. The natural conditions of the plant are not at all interfered with ; and it is protected from those circumstances arising from the refraction and concentration of heat rays by the ordinary glass, which place the foliage of the plant in an unnatural position. With this, I beg to submit to the Board a piece of the glass which I have selected. In the event of its being adopted, it would be necessary to require from the manufacturer, that no *oxide of manganese* should enter into the composition of the glass ; the effect of which would be a gradual whitening under the agency of light, which would destroy the property for which it is now chosen.

May I be permitted to remark, that my attention has been directed to a destructive influence exerted along two peculiar, and as it appears well-marked lines in the house for the orchideous plants. This, from an examination I have made, appears to arise from the actual formation of a prism of vapour along the angular roof, and I have no doubt but the lines alluded to mark out the true angles of refraction for the heating rays thus prismatically divided from the others. In all probability a roofing of green glass to this house would prevent this effect, and secure the shade which most of the orchideous plants seek for in nature. The experiment might be tried at a very trifling expense, and the result would be instructive.

I am, my lord and gentlemen,

Yours, &c.,

ROBERT HUNT.

*The Commissioners of Woods, &c.*

Office of Woods, &c.,  
21st Dec. 1846.

SIR,—I have, on behalf of the Commissioners of Her Majesty's Woods, &c., to acknowledge the receipt of your letter of the 16th instant, together with a specimen of the tinted green glass which you recommend to be adopted for glazing the New Palm House in the Royal Botanic Gardens at Kew; and as the Board are extremely desirous that this matter should be well considered, they have referred your report and specimen of glass to Sir William Hooker, for his advice, with reference to the effect upon the plants, and to Mr. Burton, with reference to the appearance in connection with the building. The Board will therefore feel obliged if you will give these gentlemen the benefit of your opinion on this subject, and conjointly with them submit a report to the Board.

I am, &c.,

[Signed] CHARLES GORE.

Robert Hunt, Esq.

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*Memorandum of the principles upon which the glass has been selected for the Palm House in the Royal Botanic Gardens at Kew.*

THE object to which my attention was particularly directed, was the selection of a glass which should not be in any way injurious to the vegetation of the plants, but which should at the same time protect them from the heat rays, which are found to permeate pure white glass, and speedily destroy the colouring matter of the leaves.

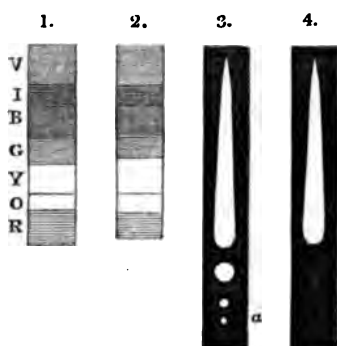
The tinted green glass, on the beneficial action of which I have the greatest reliance, having been considered by Sir Wm. Hooker, as from his experience likely to prove most advantageous in the Palm House, and being regarded as unobjectionable by Mr. Decimus Burton, it has been thought advisable by these gentlemen that the Board should be placed in possession of the principles and experiments which led me to select the glass in question.

The scorching of the leaves—the evil complained of—is due entirely to the influence of a class of Heat rays, which are distinguished by their red colour, or which exist in that portion of the prismatic spectrum where there are no Light rays.

This I have proved to be the case by experiments which have been extended over many years, and it has also been discovered by Sir John Herschel, that all vegetable colours are destroyed by that ray—the colour of which is complementary to that of the leaf or flower—hence the green colouring matter of leaves is destroyed by the red rays.

It became necessary therefore to select a glass which should not admit the permeation of the more intense heat rays, allowing at the same time

the free passage of all the others. The following figures will assist my explanation :—



*Fig. 1.* Represents the prismatic spectrum as formed by a pure flint glass prism.

*Fig. 2.* Shows the same spectrum after it has passed the glass selected for the Palm House. It will be seen that the only difference which this produces upon the rays of *Light*, is that it cuts off a small portion of the lowest red ray, and slightly diminishes the length of the yellow ray by increasing the green. By this it will be seen, that no ray is lost, and consequently no difference can be perceptible in coloured bodies viewed under this glass; the *Light* which passes it is still pure white *Light*, and we have no chromatic disturbance; a red flower, although the red ray is the most influenced, still finding enough of red *Light* to maintain its natural colour.

Sir William Herschel and Sir Henry Englefield proved the existence of the largest amount of heat in the lowest red rays, and over a space below them where no luminous rays could be discovered. Sir John Herschel confirms this, and he has proved it in a very ingenious manner. Silver paper stretched upon a frame is smoked over on one side, and being washed with ether is exposed to the action of the spectrum; under these conditions the paper dries over spaces such as are represented in *Fig. 3*. The maximum point of heat is shown by the rapid drying of the spot *a*, long before any action is exhibited on any other part, but eventually the other spots and spaces make their appearance on the paper, marking out the limits of the solar heat radiations.

By exposing leaves, and the green colouring matters of leaves, to the action of the prismatic spectrum, I find that they are rendered brown by exactly this class of rays—the browning in no instance going on beyond the orange rays, and only very slowly and faintly over the space covered by the *visible* red rays, many hours being required to produce any change under the influence of orange-coloured *Light*.

*Fig. 4.* Shows the effect of interposing the selected glass. All those heat rays which produce the scorching of the leaves are cut off, and thus the plant, by its use, would be protected from the injury complained of.

That this is the case I have proved by procuring the colouring matter from the palm leaves themselves, with which I was furnished from the Royal Botanic Gardens at Kew, by Sir William Hooker.



Several vessels filled with solutions of this colouring matter being exposed under various conditions to the influence of sunshine, it was found that those solutions which were protected by the green glass retained their colours unchanged, whilst the others exposed to the direct action of Light, or behind white glass, entirely lost colour.

ROBERT HUNT.

*The Commissioners of Woods.*

11th January, 1847.

MY LORD AND GENTLEMEN,—As it has been thought desirable to place the Board in possession of the principles upon which the green glass selected by me, and approved by Sir William Hooker and Mr. Decimus Burton, has been chosen, I have the honour to submit the accompanying memorandum as an addendum to my former report.

I have the honour to be, &c.

*The Commissioners of Woods.*

ROBERT HUNT.

#### No. V.

#### ON THE "CHEMICAL RAYS," BY M. E. BECQUEREL.

[*Referred to from pages 351. and sequel.*]

THE following extract from the memoir previously referred to will show the discrepancies in the results obtained by Becquérel in Paris, and those procured in England. Reference to the frontispiece will render the descriptions of M. E. Becquérel sufficiently clear:—

“Si l'on étend du chlorure d'argent sur du papier blanc, ou sur une surface quelconque, et qu'on l'expose dans le spectre, on voit, au bout d'un temps plus ou moins long, une réaction commencer vers l'extrême violet, entre les raies H et G de Fraunhofer, et s'étendre d'un côté dans le spectre presque jusqu' en F dans le bleu, et de l'autre bien au delà du violet visible; mais si le chlorure d'argent, après avoir été préparé dans une chambre parfaitement obscure, est exposé pendant un temps très-court à la lumière diffuse ou solaire, mais de manière à ce qu'il ne soit pas noirci, mais qu'un très-faible commencement d'action ait en lieu, si on le place après dans le spectre, on voit non-seulement une coloration vers le violet extrême, mais encore une action se manifester en même temps dans la partie la moins réfrangible du spectre jusqu' au rouge extrême, de sorte que l'espace noirci se trouve dans toute l'étendue du spectre lumineux, et bien au delà du violet. D'après le mode d'action de la lumière, j'avais nommé les premiers rayons situés vers le violet *rayons excitateurs*, et les autres *rayons continueurs*, parce qu'ils continuent une action chimique commencée sous l'influence des premiers. —Ainsi, lorsque le chlorure a été primitivement un peu impressionné, l'étendue de la partie colorée se trouve depuis le rouge extrême, jusque bien au delà du violet, mais il y a deux maxima d'intensité d'action, l'un entre G et H, l'autre entre D et E, vers le jaune, et correspondant aux rayons continueurs.—Si l'on emploie du bromure d'argent préparé par double précipitation au bien par double décomposition sur du papier en

étendant un bromure soluble, puis du nitrate d'argent on obtient les mêmes effets, se ce n'est que l'action s'étende plus ou moins loin au delà du violet, et que les maxima ne sont peut-être pas aux mêmes places; mais si'il y a une différence, elle est très-faible. L'iodure d'argent, et en général presque tous les sels d'argent, éprouvent la même action de la part des rayons solaires; les plaques d'argent iodurées à la manière de M. Daguerre, et même rendues plus sensibles à l'aide du chlore et du brome, éprouvent les mêmes réactions, si ce n'est que les rayons excitateurs s'étendent un peu plus ou un peu moins loin; et même on a remarqué que les maxima changent un peu de place, de sorte qu'en employant telle ou telle préparation d'argent, la position du maximum des rayons excitateurs n'est pas la même; mais ils sont généralement situés, entre H et G, et entre D et E. \* \* \* Si, au lieu de placer dans le spectre des papiers ou des surfaces enduites de matières impressionnables formées avec des sels d'argent, ou place un papier préparé avec du bichromate de potasse, alors, au bout de quelque temps, on voit une réaction commencer vers F à la limite du vert et du bleu, puis s'étendre d'un côté en E, et de l'autre au delà de H vers M, de sorte que le maximum a lieu vers E.

Si l'on emploie un papier enduit de résine de gaïac, on le voit bleuir au delà de H, le maximum étant vers M; si au contraire, on place dans le spectre du gaïac bleui à la lumière, alors le gaïac redevient blanc dans le spectre, depuis le rouge A jusqu'en H le maximum étant vers F.—(*Annales de Chimie et de Physique*, November 1843.)

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No. VI.

ON THE DISCOLORATION OF PHOTOGRAPHIC PAPERS BY ELECTRICITY, AND THE PRODUCTION OF ELECTROGRAPHS.

[*Referred to from page 265.*]

M. AUG. PINAUD has studied the action of static-electricity on the chloride, iodide, and bromide of silver, comparing it with the action of Light on the same bodies. A notice of these researches has appeared in the "Comptes Rendus." He has found that electricity proceeding from a point, whether positive or negative, imparted brilliant spots of a bluish colour to the ioduret of silver on a prepared Daguerreotype plate, and by this means all sorts of figures can be traced upon it. M. Matteucci has shown that an instantaneous escape of electricity, without *visibly* affecting a silver plate, occasions on its surface a deep and lasting alteration, which is rendered evident by the condensation of the breath or any vapour on the plate. The vapour condenses around the part which has received the electricity, and tarnishes the metallic surface, but the points, which have been acted on by the electric fluid, remain bright. This fact serves to confirm the position I have maintained in opposition to Möser, that the condensation of vapours may be effected by other influences than Light. M. Pinaud exposed paper pasted on an insulated metallic plate and covered with dry bromide of silver to the action of electricity from a very

fine metallic point electrized *negatively* by induction. Opposite the point a spot of a blackish brown colour is immediately formed. By passing the point over the paper any figure can be sketched out. The discoloration thus obtained has a deep brown shade like that produced by Light. If the metallic point touches the paper, the discoloration is then a deep black, and limited to the points which are touched; and the effect is that of a black-lead pencil. Positive electricity does not appear to produce any effect upon the bromide of silver. On the nitrate of silver and the chloride the electric fluid effects but little change; iodide of silver on the contrary is, when spread over paper, readily changed by either positive or negative sparks; the negative spark forming a round black spot, the positive developing in all the filaments of the paper, amongst which it is diffused, a violet discoloration in a radiated form. If paper covered with the iodide of silver is placed upon the insulated stand of a universal discharger, and the spark of a highly-charged jar is passed from point to point along a distance of an inch or two, the trace of the spark is instantly impressed upon the paper by a reddish train, which records all its windings and sinuosities.

Another method adopted by M. Pinaud for obtaining electric pictures is, to place a sheet of dry iodized paper upon a spotted glass plate, and retain it by means of a glass plate slightly pressed against it. The discharge of a powerful Leyden jar is then passed along the metallic ribbon, and each space is marked by a spark, and spots are formed on the paper at all the corresponding points. The analogy between these phenomena and those produced by solar agency are striking, and they well deserve investigation.

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#### No. VII.

#### THE NON-EXISTENCE OF ANIMAL AND VEGETABLE LIFE IN THE DEPTHS OF THE OCEAN.

[*Referred to from page 353.*]

PROFESSOR FORBES, of King's College, London, who was engaged during eighteen months on researches in the Ægean Sea and on the coasts of Asia Minor, during which time particular explorations of the sea bottom were made by means of the dredge, has defined the depths at which various species of animals and vegetables exist. He has proved by the decisive evidence of actual examination that, below the depth of thirty-five fathoms, the number of animals diminishes as we descend, until at the depth of about 200 fathoms the number of testacea was found to be only 8, and a zero in the distribution of animal life was indicated at probably about 300 fathoms. Green fuci were not found below 55 fathoms, and millepora not deeper than 105 fathoms. I am informed by my friend, Mr. Richard Couch of Polperro, who has exhibited the most indefatigable spirit in his researches around the south coast of Cornwall, that he has found the same law to be maintained over this portion of the British Channel. Vegetable and animal life ceases at about the same

depths as in the *Ægean Sea*. We may therefore infer that this condition is maintained, or nearly so, over every part of the ocean. Professor Forbes and Mr. Couch have, both of them, remarked that the vegetables and animals near the surface of the sea are brilliantly coloured, but that they gradually lose the brightness of their hues as they descend, until the animals of the lowest zone are found to be nearly colourless. Hence we see the dependence of marine, animal, and vegetable life upon the solar influences, to as great an extent as over the surface of the dry land. M. E. Becquérél's position is not a good one, and it affords us no evidence that any marine animal has the powers of vision under the influence of such rays of Light as would not excite the optic nerve of man. Organisation and life exist only at the surface of our planet, and under the influence of Light. Those depths of the ocean at which an everlasting darkness prevails is the region of silence and eternal death.



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